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HEMICAL ENGINEERING SERIES

PETROLEUM REFINERY ENGINEERING

BY

W. L. NELSON

Consulting Petroleum and Chemical Engineer, Professor of Petroleum Refining, University of Tulsa

SECOND EDITION
FIFTH IMPRESSION

McGRAW-HILL BOOK COMPANY, INC.
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PETROLEUM REFINERY ENGINEERING

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PREFACE TO THE SECOND EDITION

Only a few minor processing operations have been abandoned since the First Edition of this book was published, but improvements in the accuracy of physical constants and the development of new processing methods make a Second Edition necessary. In addition to bringing material up to date, new chapters entitled "Rebuilding Hydrocarbons," "Auxiliaries to Processing," and "Solvent Treating or Extraction Processes" have been added as well as entirely new material on multiple-component fractionation, catalytic processes, and solvent dewaxing.

The conversion, by means of chemical reactions, of the bulk of petroleum into new and different products from those normally found in crude oil is the major achievement of the past six years. Heretofore, the processing of petroleum has been largely by means of physical processes except for the classic example of cracking or thermal decomposition. The gaseous hydrocarbons of 2 to 4 carbon atoms have been the raw stocks for most of the newly developed processes, but there is justification to hope that in time nearly all of the hydrocarbons in petroleum will be identified and made available for synthesis into uniquely valuable new materials.

W. L. NELSON.

TULSA, OKLA.,
October, 1941.

PREFACE TO THE FIRST EDITION

There are many valuable reference books pertaining to petroleum refining and the derivatives of petroleum, but as yet there has been no adequate presentation of the fundamentals of engineering design and processing. It is my hope that this book will aid in clarifying the many detail questions that arise during plant operation and that the book will encourage the refinery engineer to utilize the principles of chemical engineering more fully. The book should be of value to engineering students; to plant superintendents, engineers, chemists, and foremen; and to scientists who may wish to follow the application of their theoretical work. Aside from petroleum refining, the book should be of interest to chemical engineers because of refinery practice that may be applied to other industries.

I regret that much useful information could not be discussed. Subjects such as corrosion, pipe and fittings, pumping equipment, engineering and plant economics, control instruments, and structural features are of vital importance, and they deserve more attention than this volume permits.

Engineering involves the practical application of scientific knowledge, and hence I have made a conscious effort to emphasize the practical phases of engineering work. In so doing it has often been necessary to resort to empirical relationships. No apology is necessary for such a treatment, because engineers must build and operate plants regardless of inadequate information. In fact the history of industrial development shows that commercial plants are usually built before the theory of the process is fully understood. Scientific study follows the empirical development, and science finally administers those fine improvements which stamp the new process as truly great. The process of empirical growth will always be the lot of the practical scientist or engineer.

For the same reasons some handbook information has been introduced. Although such information is not profound, it is the tool by which theory can be put into action. Such information is also necessary in the solution of illustrative problems, and I believe that no method of engineering study is more effective than detailed examples. Furthermore, an engineer must spend more time applying information than deriving or finding it, and hence handbook information and comprehensive references are provided. The current literature contains much that is useful, but the literature is so voluminous that it may be useless to a busy engineer unless it is presented in an organized form. I have attempted to organize this contemporaneous literature, but I have refrained as far as possible from tiring the average reader with too many references and conflicting opinions.

By this practical approach I hope that the book will make our inadequate fund of information more useful to the engineer. The book deals mainly with design fundamentals, and it should complement and supplement other valuable petroleum books which deal with other phases of refining, such as Redwood's "Treatise on Petroleum"; Nash and Howes' "Principles of Motor Fuel Preparation"; "Petroleum Technology," by Gurwitsch; and "Chemical Refining of Petroleum," by Kalichevsky and Stagner. Doubtless, the design methods here outlined will not always coincide with the methods used by other engineers, but by means of this structure of design methods we should all be able to gain a larger insight into petroleum processing.

I find it difficult properly to acknowledge all of the contributions to this volume. I am particularly indebted to Professor A. H. White of the University of Michigan, for inspiration and an appreciation of engineering endeavor, to Dr. S. Born of the University of Tulsa for a close cooperation in many phases of the work, and to Dr. G. G. Brown of the University of Michigan, because of frequent references to his valuable work on natural gas and petroleum.

I am indebted to Dr. Gustav Egloff of the Universal Oil Products Company, Dr. R. J. Kaufmann of the University of Tulsa, Mr. L. L. Davis of the Continental Oil Company, and Professor Walter G. Whitman of the Massachusetts Institute of Technology, for advice concerning parts of the manuscript.

W. L. Nelson.

Tulsa, Okla.,
January, 1936.

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PETROLEUM REFINERY ENGINEERING

CHAPTER I

CHEMICAL ENGINEERING AND PETROLEUM ENGINEERING

The refining of petroleum constitutes one of the important branches of chemical engineering. The industry utilizes most of the unit operations of chemical engineering, and much of the modernization of the industry during the past decade can be attributed to the adoption of chemical engineering principles. The chemical engineer differs from the industrial or plant chemist in that he is trained as an engineer in the construction and operation of commercial chemical equipment, and he differs from the mechanical engineer because he has a more thorough training regarding the chemical and physical changes that occur. Thus, chemical engineering deals with processing operations, and petroleum refining is a typical process industry. Among the unit operations that are most widely used are fluid flow, heat transfer, distillation, absorption, filtration, and extraction. Some of the purely chemical operations are treatment with sulfuric acid and with alkalies, percolation and contacting with fuller's earth, cracking or thermal decomposition of heavy oils into lighter ones, and hydrogenation. The number of chemical engineering graduates that enter the petroleum industry is clear proof of the close relation of chemical and petroleum refinery engineering. In recent years more chemical engineering graduates have found employment in the petroleum industry than in any of the other chemical industries, such as organic chemicals, heavy chemicals, rubber, iron and steel, fertilizers, and leather. The petroleum industry is also said to be the largest single market for chemicals. Considering the sale of sulfuric acid, alkalies, fuller's earth, tetraethyl lead, alcohol and other chemicals as antifreeze materials, organic liquids for solvent extraction, and the many other chemicals that are used, the total market at the present time amounts to more than $100,000,000 a year.

Design and Operation.—The chemical engineer, by virtue of his training, is particularly qualified to supervise the design and operation of manufacturing equipment. The fundamentals of design and the fundamentals of plant operation are the same, and hence a designer cannot hope to be entirely successful unless he is an experienced operator, and conversely a plant cannot be operated most successfully or economically without a knowledge of design. In fact the very methods by which a plant is designed are the same as those used by an operator when he analyzes the behavior of the plant.

In many ways the operation of an equipment may be more difficult than the design of the equipment. The designer is somewhat removed from many practical problems, and regardless of his ability he will be unable to anticipate all of the factors that may appear during operation. The operator cannot avoid these factors—he must meet them in actuality, and his task is an endless one. Thus, plant operators, superintendents, and even plant executives are interested in equipment design because it is so closely related to plant operation.

Plant Development.—The training of the chemical engineer also fits him for the economic study of processing operations and the development of new processes. Perhaps this accounts for the large number of chemical engineers that are employed as business executives. The development of a new process embraces the broadest type of knowledge. The process must be based on sound scientific principles; methods and equipment must be devised by which the process can be carried to a commercial scale; and—of prime importance—the process must be economically feasible. A knowledge of the unit operations of chemical engineering is the tool by which new processes may be transferred from the laboratory to full-scale commercial equipment.

CHAPTER II

HISTORY AND DEVELOPMENT OF REFINING

Coal oil for household lamps was already being manufactured in the United States when the Drake discovery well (1859) was drilled. In 1846 Dr. Abraham Gesner had prepared coal oil from coal by thermal decomposition, and he lectured upon its manufacture and use. The country was truly interested in coal oil because sperm oil was becoming more and more expensive. The number of coal-distillation plants in the United States during the years 1852 to 1859 has been estimated as 60. The largest of these was the Downer plant which involved an investment of $250,000. This industry was thrown into confusion by the discovery of petroleum in Pennsylvania, and within a few years most of the coal-distillation plants had been adapted to the processing of petroleum. Although records show that petroleum was distilled in Russia in 1735,[1] the first real refinery is generally conceded to be that of William Barnsdall and William H. Abbott. This plant was built at Titusville, Pa., in 1860 at a cost of $15,000. Hundreds of small refineries, having daily capacities of 10 to 500 bbl., and several larger ones were in operation by 1873.

Continuous Distillation.—All the earliest refineries operated by the batch system of operation. In this method a quantity of oil was charged into a vessel, and the products were distilled, one by one, by raising the temperature until a residue of heavy lubricating oil or tar remained in the still. Although the batch method survives even today in small plants, enterprising refiners soon recognized the advantages of continuous operation. In 1860 a patent was granted to D. S. Stombs and Julius Brace disclosing the essentials of a continuous system. In such a process the crude oil is admitted to the plant continuously, and the products are collected continuously therefrom. Batch or intermittent processing with a cycle consisting of (1) charging, (2) operation, and (3) shut-down is wasteful of labor, material, and fuel. Truly successful continuous plants were not in operation until after the patents of Hill and Thumm of Oil City, Pa., in 1870; of Van Syckles of Titusville, Pa., in 1877; and of Norman H. Henderson, an Englishman, in 1889. Although the M. J. Trumble patents (1911) are usually considered as an innovation in fractionation, nevertheless they involve the use of a continuous tubestill heater and disclose the conception of modern continuous distillation. The first successful Trumble plant was built at Vernon, Calif., in about 1912 by the General Petroleum Corporation. Since that time the tubestill or pipestill has been finding increasing usefulness. As will be discussed later, the pipestill is necessary if the principles of fractionation in a bubble-tower are to be completely utilized. The pipestill has the further advantage that it allows an absolute control of the velocity of the fluid past the heating surface. The advantages of circulation have long been recognized even in shellstill practice. The Hill and Thumm patent of 1870 specifies that the oil shall flow continuously in a thin stream over the heating surface, and more recently C. W. Stratford introduced a shellstill with a manifold of nozzles arranged along the bottom of the still. Modern distillation plants are completely continuous, with the exception of cokestills which are operated either as batch or as semi-continuous operations. In modern plants several distillation units are often connected together so that the hot product from one unit (usually the residue) is pumped directly to another. Also, several units may have a common heat-exchange system by which the charge stock for one unit is heated in other units. In other phases of refining, such as treating; dewaxing, compounding, and packaging, the processing is still partly batch or semi-continuous, but continuous operation is not of great value in these operations.

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[1] Herodotus (450 B.C.) and other historians report petroleum and tar (under other names) at dates before 1735, but they do not tell how the oil was refined.

Cracking or Thermal Decomposition.—Even the phenomenon of cracking is not a modern development. True, the large plants and the wholesale manufacture of decomposition products are new, but thermal decomposition was actually practiced in the distillation of coal and oil shale even before the days of the oil industry. During the first years of the petroleum industry a "cracking distillation," in addition to the customary distillation with steam, was practiced. The cracking distillation is reported to have been discovered accidentally in 1861. A distillation in a 16-bbl. still had been half completed, and the stillman had built a strong fire. The stillman intended to be away an hour but was unable to return until 4 hr. later. He found that a light-colored distillate of a low specific gravity was being collected. The specific gravity was even lower than that of the product before he left. Upon investigation, it was found that a heavy oil was condensing on cooler parts of the equipment and dropping back into parts of the still that were at a temperature sufficiently high to cause decomposition of the heavy oil into lower boiling-point products. In the early days of the industry gasoline was of little value, and cracking was practiced for the purpose of producing more kerosene than could be obtained by steam or simple distillation. The first attempts to produce gasoline by cracking were by the decomposition of petroleum vapor. Although none of these first attempts were commercially successful, they are worthy of mention. Early patents in vapor-phase cracking are those of Greenstreet, Rittman, Alexander, Hall, Parker, the General Petroleum Corporation, the Texas Products Company, Ramage, and others. However, vapor-phase plants were not entirely successful until about 1925. At that time the Gyro and de Florez processes were being developed.

Refinery statistics*	1931	1941
Operating capacity, U.S. bbl. per day	3,913,180	4,524,775
Cracking capacity, U.S. bbl. per day. .	1,844,609	2,276,200
Percentage of oil cracked.	47.2	50.2
Cracked gasoline, percentage of total†	40.0	47.8
Number of operating refineries.	397	459
Foreign capacity, bbl. per day.	2,051,300	3,202,885‡

* *U.S. Bur. Mines, Statistical Econ. Surveys* and *Oil Gas J.*, Mar. 27, 1941.
† Preliminary figure for 1940 from "Facts and Figures" of the A.P.I.
‡ Figure for 1938.

The liquid-phase cracking processes were the first to be commercially applied, and the Burton process was the first to be practiced on a large scale. Development began in 1910; a patent was issued in 1912; recognition of Dr. Burton by the

Willard Gibbs Medal was given in 1918; and by 1921 over 800 Burton stills were said to be in operation. Other early liquid-phase processes were the Fleming, Isom, and Emerson processes.

The importance of cracking in the modern refinery may be emphasized by a few statistics as shown in the table on page 5. Although the names of cracking processes have lost much of their significance, the following is a list of the approximate daily capacities of cracking plants proposed and/or completed during 1938–1939 as recorded in "The Cracking Art in 1938 (and 1939)" by the Universal Oil Products Company of Chicago, Ill.:

CAPACITY OF CRACKING PLANTS INSTALLED IN 1938–1939*
In barrels per day of charging stock

	United States	Foreign
Houdry and other catalytic	252,500	13,100
Dubbs	54,745	51,110
Combination and others	164,500	255,750
Total	471,745	319,960

* Complete information is not available; 150,000 tons of crude and cracking capacity installed in Russia is not listed.

The general scheme of processing is much the same in all modern cracking plants. The advantages of cracking only those stocks which contain no cracked tar is recognized by all. A residual charge-stock is often distilled in the cracking unit itself, but only the distilled part of the stock is exposed to cracking conditions. However, residual stocks are cracked directly in some processes. These processes usually produce a slightly larger yield of gasoline, but the length of time on stream may be short. Another generally recognized advantage is the use of a quench-stock to cool the cracked material rapidly from the cracking temperature to a temperature low enough to avoid the deposition of coke. All systems are continuous, unless coke is being produced.

The newest developments in cracking are "viscosity-breaking" plants and "reforming" plants. In the first of these only a mild decomposition takes place. The purpose is to decompose the oil just enough to lower its viscosity and pour-point, so that it can be pumped more easily. Little or no gasoline is produced. Reforming units are cracking plants that operate on naphtha or low-octane-number gasoline. The naphtha is decomposed into a large percentage of highly antiknock gasoline. These units were developed in response to the growing demand for the antiknock gasoline that is required for modern automobile engines. Although hydrogenation may not belong under the heading of cracking, it is so similar to cracking that it should be mentioned at this point. Since 1927 the process of hydrogenation, as developed by the Standard Development Company, has attracted much attention. This process differs from cracking mainly because of the introduction of hydrogen, in the presence of a catalyst, into the decomposition zone. Assimilation of hydrogen occurs at elevated pressures and temperatures. The process may be adapted to the manufacture of most of the commercial oil products, whereas cracking is practiced only for the manufacture of gasoline. In the future we may expect that the hydrogenation plant will be the very nucleus of refinery processing.

Fractionation.—The term fractionation refers to the separation of a liquid mixture into several products of shorter boiling-range by means of vaporization. In early refineries this separation was obtained by a series of distillations in which, first, an inaccurate separation was made and then the partly separated products were redistilled several times, if necessary, until finally the product met market requirements. The next development was to fractionate by partial condensation; *i.e.*, a mixture of vapor was condensed in portions by successively cooling the vapor to lower and lower temperatures. An invention of this nature was that of Hugh L. Allen (Eng. Pat. 117,277–1918) in which the vapor was successively cooled by means of a series of air-cooled condensers into several liquid products. This type of separation, although it is practiced even today, has not proved to be widely useful.

The modern era of refining dates from the adoption of pipestills and bubble-towers. The name bubble-tower has become common because the vapor in the tower bubbles through the liquid on the plates in the tower. In bubble-tower fractionation a mixture of ascending vapor is scrubbed by a descending flow of oil. Bubble-towers have been so universally adopted, all within a few years, that no one can be accredited with invention. In fact the fundamentals of fractionation were borrowed directly from the chemical distillation industries.

Bubble-tower fractionation is the standard method of separation used in all phases of modern refinery distillation. Bubble-towers are used in topping plants, rerun plants, vacuum plants, cracking plants, natural-gasoline stabilizers, absorption plants, and steam stripping operations.

Natural-gasoline Plants.—Natural gasoline attracted little attention until about 1912, at which time the demand for motor fuels became acute. Today more than 7 per cent of all the gasoline produced is manufactured from natural gas. The first widely used method of recovery was the compression process. As gas is compressed, the dew-point is raised so that, upon cooling to the original temperature, a mixture of hydrocarbons condenses. The condensate contains a large percentage of volatile hydrocarbons, such as propane, which must be removed before the gasoline is a suitable motor fuel. The first method that was used to remove these hydrocarbons from the raw gasoline was called "weathering." Weathering was accomplished by allowing the "wild" gasoline to stand in an open vessel for a time. A large part of the gasoline was lost during this weathering.

In later processes, natural gas was passed through absorption chambers or packed columns, in which the gasoline was absorbed by naphtha. These naphtha-columns finally developed into the absorption process of today. In the absorption process the natural gasoline is absorbed by a low-boiling-range gas oil, and the gasoline is recovered from the rich gas oil by heating it and stripping the gasoline from it with steam.

For a few years following the First World War the *adsorption* process received much attention, but since that time it has been almost abandoned. In this process the gasoline was adsorbed by charcoal and recovered from the charcoal by steaming.

The high-pressure absorber is one of the newest developments in natural-gasoline manufacture. Much smaller quantities of absorption oil are required. Usually it does not pay to compress the gas, so that high-pressure absorption is usually limited to the processing of those gases which are already at a high pressure at the field. Natural gasoline is no longer weathered. The wild gasoline is stabilized by fractionating it at a pressure of about 150 lb. per square inch in a fractionating or stabilizing column.

Dewaxing.—The filter-press method of dewaxing, as originally used in Scotland for shale oil before the development of the oil industry, is still the most widely used method (1939) of dewaxing the lighter wax-bearing oils. Heavy residual wax-bearing stocks were first dewaxed by cold-settling. The early refiners discovered that a waxy layer of oil was deposited in the bottoms of crude-oil storage tanks, if the tanks were allowed to stand full of oil through the winter. The cold-settling method was a development of this practice. The oil was chilled and allowed to stand in insulated tanks. The centrifuge process of dewaxing residual stocks was studied for many years before it was entirely successful. The difficulty had been the obtainment of sufficiently high centrifuge speeds and the removal of the petrolatum wax from the bowl of the machine. In about 1921 warm water was suggested as a carrying liquid to be injected at the edge of the bowl. The use of warm water was successful, and the centrifuge method of today is essentially the same process as was then used.

Recently, solvent dewaxing methods have become important. An important advantage of these processes is the ability to handle both light and heavy wax-stocks by a single process. Many different solvent processes are being practiced commercially, but as yet no one process has been accepted to the exclusion of others.

Chronology of Market Demands.—In the following outline no attempt has been made to set the date at which new processes were conceived. Developments are not mentioned until the time when they were generally accepted by the industry.

1860 to about 1885.—The major refinery product was kerosene or burning-oil. During this period disfavor was brought upon the industry by the sale of burning-oils that contained too much gasoline. Laws were enacted limiting their flash-point.

1885–1900.—Mineral lubricating oils gained favor with the public. Until this time vegetable oils were considered the best. Paraffin-base lubricating oils gained a favorable reputation which has been retained to this day.

1900–1914.—Shortly after 1900 gasoline began to be valuable, and within a few years it had grown to be the most useful refinery product. The demand became so great that many new oil fields were discovered, and fundamental improvements in refining methods ensued. The compression process for the recovery of natural gasoline was developed, and experiments were conducted concerning cracking.

1914–1925.—The ever-increasing demand for gasoline caused the refiner to turn to methods of recovering more of it from crude oil. The cracking processes were brought to a high degree of perfection, and the fundamentals of heating, fractionation, heat transfer, and absorption were developed and put into practice. Continuous processing systems using fractionating towers, pipe- or tubestill heaters, and heat exchangers were developed. Structural equipment was developed for high pressures and high temperatures. In 1920 a marked increase in the use of fuel oil for the generation of power was noted, and the tendency has continued until today.

1925–1929.—During this period the large profits from lubricating-oil processing attracted attention, and vacuum distillation was developed. Until this time vacuum distillation had not been truly successful, because batch or shellstill heating had to be used. The newly acquired knowledge of pipestill and fractionating-tower design made the development of continuous vacuum-distilling systems a logical step. Low cold-test oils were produced by direct expansion of ammonia rather than by the customary method of circulating brine. Continuous pipestill equipment was adapted to all distillation operations including the rerunning of pressure-distillate and lubricating-oil stocks. The Edeleanu method of solvent treating proved to be commercially successful.

1929–1935.—The demand for highly antiknock gasoline resulted in the development of vapor-phase cracking plants, gasoline-reforming units, and an ever-increasing use of cracking plants. The hydrogenation process was developed, but it has not been widely used because of unfavorable economic conditions. Several successful solvent-dewaxing and solvent-treating methods were developed. High-viscosity-index lubricating oils are produced by solvent-treating methods. Vacuum distillation was widely applied to the manufacture of road oil and asphalt.

1935–1941.—Polymerization, dehydrogenation, and alkylation processes were applied to the hydrocarbons propane and butane which are found in natural gas. These processes provided a source of unsaturated hydrocarbons that was increasingly useful in developing a petroleum chemical industry. Catalytic cracking processes which utilize a catalyst to assist and control the cracking of petroleum were introduced and along with the preceding processes permitted the manufacture of 100 octane number airplane fuel. Most manufacturers prevented the formation of gum in cracked gasoline by the use of inhibiting agents—and colored gasolines were generally accepted by the public.

The Magnitude of the Industry.—The "Biennial Census of Manufactures" and the "Statistical Abstract of the United States," both by the Department of Commerce, indicate that the manufacture of petroleum (and coal) products is of national importance. In the year 1939, by value of plant products, petroleum and coal products ranked fourth among the 16 major groups of industry.

Compared with individual manufacturing industries, petroleum refining commands an even more important position. By value of products in 1939, the motor-vehicle industry ranks first at a value of $4,039,930,733; steelworks and rolling-mill production valued at $2,720,019,564 is second; and wholesale slaughtering and meat packing is third with $2,648,325,552, closely followed by petroleum refining with products valued at $2,461,126,549.

In 1890 the value of refinery products was about $85,000,000 per year, and by 1937 about $2,546,746,000. In 1939 there were 463 operating refineries in the United States having a daily capacity of over 4,000,000 bbl. per day. The industry grew rapidly from about 1912, at which time the demand for gasoline became important.

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CHAPTER III

INTRODUCTION TO PROCESSING

There are three general types of crude oil, *viz.*, *paraffin* base, *mixed* base, and *naphthene* (asphalt) base. These classes and their identification will be discussed in detail in Chap. VII. The student should beware of attaching too much importance to this classification, but it is useful to men of wide experience. Crude oil varies greatly in composition, so that no definite grouping is possible. In general the oils fall into the foregoing classes, but few oils are typically paraffin, naphthene, or mixed base.

Variety in Processing Methods.—Because of the differences in crude oils, we find that processing methods differ. We may safely say that no two plants are employing exactly the same processing scheme. What may be a perfect method of handling one oil may be inadequate for another. The refining of an oil is, of course, an economic problem. (1) What are the value and the accessibility of the raw stock; (2) what are the value of the products and the possibilities of marketing them; (3) what yields of products are to be expected; and (4) what will it cost to process the stock? These factors promote the use of many different processing plans.

Refinery Products.[1]—A study of the products of refining will help to show why so many different processing methods are used. The more important refinery products may be grouped as follows:

1. *Natural and refinery gas*—household and industrial fuel.
2. *Gasoline*—fuel for internal-combustion engines.
3. *Naphtha and benzene*—cleaner's solvents, paint thinners, chemical solvents, and stocks for the blending of motor fuels.
4. *Kerosene*—burning-oil for household lamps.
5. *Distillates and gas oil* (distilled products)—fuels for industrial and household furnaces, enriching agents in gas manufacture, and absorbents for hydrocarbon gases.
6. *Neutral oils*—light or low-viscosity lubricating-oil stocks for the compounding of motor oils.

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[1] See Chap. IX for details.

7. *Brightstock*—heavy or high-viscosity lubricating-oil stocks for the compounding of motor oils.
8. *Cylinder oils*—unfinished heavy-oil stocks used directly as lubricants for steam-engine cylinders or for the manufacture of brightstock. Usually filtered but not dewaxed.
9. *Paraffin wax*—used for the manufacture of wax paper, insulating material, package sealing, etc.
10. *Petrolatum* (noncrystalline wax)—base material in the compounding of greases, salves, and ointments.
11. *Fuel oil* (residual product)—industrial fuel.
12. *Tar and asphalt*—asphalt, road oil, roofing materials, and protective coatings.
13. *Petroleum coke*—solid industrial fuel.

General Processing.—The most important method of separating petroleum products is distillation, and hence the products should be compared with one another in the order of their boiling-ranges. A mixed-base oil might yield products as indicated in Fig. 1. Figure 2 likewise indicates the relation among the raw

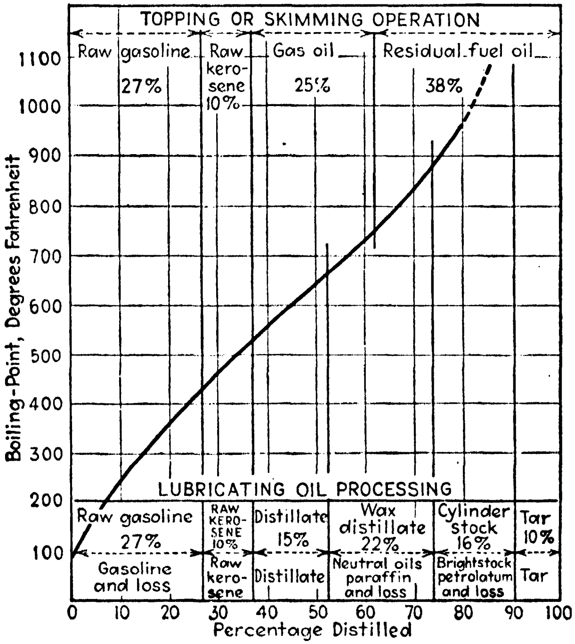
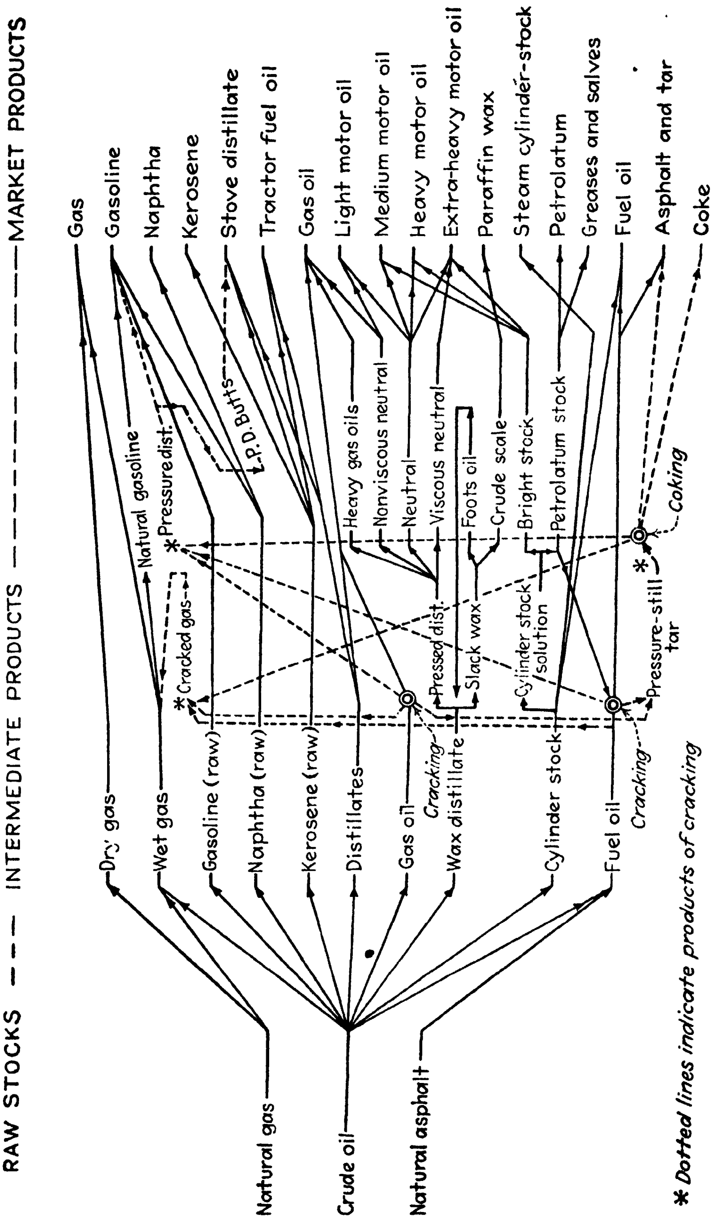


FIG. 1.—Boiling range of refinery products (31.7 A.P.I. Texas mixed-base crude oil).



Dotted lines indicate products of cracking

FIG. 2.—Relation between finished, intermediate, and raw products.

materials, the intermediate refinery stocks, and the finished market products. The dotted lines indicate products obtained by cracking. The products obtained by distillation are called raw products, and most of them cannot be sold until they have been further refined.

Raw gasoline and raw naphtha are often treated with chemical agents such as sulfuric acid, sodium hypochlorite, or certain earths. Kerosene usually requires only a sweetening treatment; but for fine colors, acid treatment or filtration is used. The distillate fuels and gas oil are usually sold without being refined, but when used for special purposes they are also treated with sulfuric acid. *Pressure distillate* or pressure gasoline, obtained by cracking or thermal decomposition (Fig. 2), may be treated with acid and redistilled or treated in the vapor-phase with fuller's earth. *Natural gasoline*, obtained from natural gas, usually requires only a sweetening treatment for the removal of hydrogen sulfide.

Wax distillate, the raw stock for the manufacture of the light lubricating oils or neutral oil-blending stocks, contains crystalline wax. The wax is removed by chilling the distillate and filtering the wax from the oil in filter presses. Two unfinished stocks, *slack wax* and *pressed distillate*, are obtained in the pressing operation. *Neutral oils*[2] are produced from the pressed distillate by distillation and subsequent filtration through fuller's earth. Crude scale is produced from slack wax by "sweating" or, in other words, by slowly warming the chilled slack wax so that the oil and low-melting materials, which together are called *foots oil*, melt and drain from the slack wax. Crude scale is slightly yellow in color, and this coloration may be removed by treatment with acid or caustic or by filtering the melted wax through clay. Cylinder stock is another wax-bearing product, but the wax is such that it cannot be filtered from the oil in wax presses. This so-called amorphous wax or *petrolatum stock* may be removed by dissolving the oil in naphtha, filtering the solution to a proper color through fuller's earth, and centrifuging the chilled solution in high-speed centrifuges. The products from this separation are solutions of *brightstock* and *petrolatum*. The naphtha is removed from the solutions by distillation, leaving finished brightstock and petrolatum.

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[2] The neutral oils are often referred to as pale or red oils. In the past it was thought that part of the wax distillate had to be cracked to produce a pressable material, and the neutrals from the cracked distillate, being a deep-red color, were called red oils. The terms have now lost their original significance, and the term red oil is usually reserved for any neutral oil that is darker than 3 N.P.A.

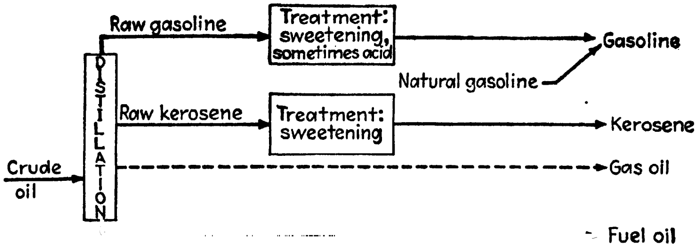
Cracking Distillation.—Materials such as *cracking-still gas*, pressure distillate, *cracked gas oil*, and *pressure-still tar*, which are the products of cracking, have already been mentioned. By cracking we refer to the decomposition of heavy or high-boiling oils by heating. At temperatures exceeding about 680°F. materials such as gas oil, fuel oil, and tars are decomposed into (1) gas, (2) volatile materials (pressure distillate) having the same boiling-range as gasoline, and (3) a residue of heavy material (cracking-still tar) or coke. Pressure distillate receives its name by reason of the high pressures that are usually maintained in the cracking equipment. Cracked gasoline from pressure distillate is highly valued as an ingredient of the superior antiknock motor fuels. Likewise the residue, if cracking is not conducted to the ultimate formation of coke, is called pressure-still tar.

Recycle stock or cracked gas oil, an intermediate between the two foregoing products, is also produced. Recycle stock has about the same boiling-range and about the same physical characteristics as gas oil. This material is normally recycled through the cracking system so that it is completely used in the cracking reaction, but a part of it is sometimes sold as distillate or gas oil.

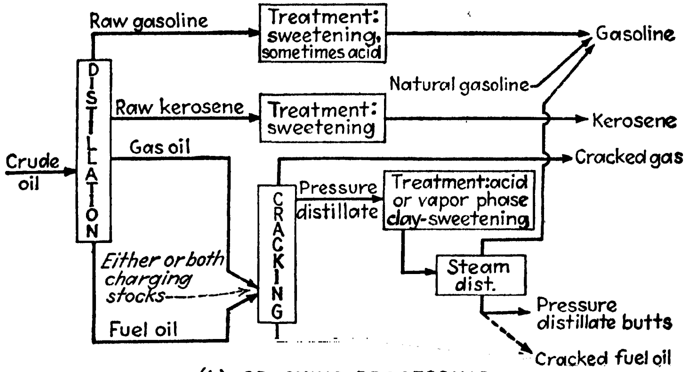
Summary.—In general the refining of petroleum is carried out as outlined in this chapter. However, crude oils vary widely in their properties, and some may not yield all the foregoing products or may contain such small amounts of certain of the products that their manufacture is not profitable. Likewise, certain oils are inherently superior to others and may not need the treating of finishing operations as outlined, but others may need an even more vigorous chemical treatment. Still further, the particular market conditions that each refiner must meet are an important factor in governing the extent of the refining operations. Certain localities have become accustomed to using discolored gasoline; others demand a white gasoline; and still others prefer a dyed gasoline, to which the coloring matter may have been added for the express purpose of masking the yellow color and simplifying the refinement. Likewise, in certain rural districts the customer will not buy a light-colored motor oil because he fears that the oil is not viscous, whereas in the city the darker colored oils may be considered as insufficiently refined. All of these factors tend to create a large number of different processing methods.

In general, paraffin-base raw products are the most easily treated, and the others follow in the order mixed-base and naphthene-base. This applies to the light distillates such as gasoline, as well as to the heavy lubricating oils. Naphthene-base oils usually contain more *sulfur* than mixed-base oils, and paraffin-base oils may contain scarcely any sulfur. Paraffin- and mixed-base crude oils contain wax, and this must be removed in producing finished market products. The fact that a true naphthene-base oil contains *no wax* simplifies the manufacture of lubricants.

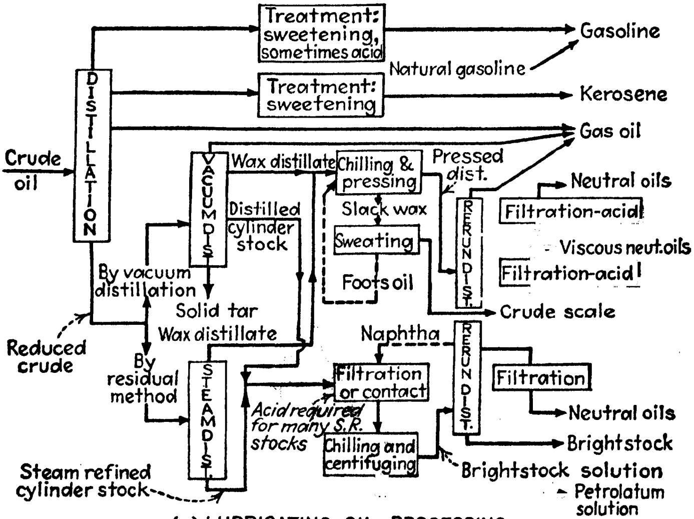
These characteristics govern the methods of processing that are used for the different bases of oils and the products that are manufactured. Paraffin-base oils are particularly suited for the manufacture of lubricating oils. However, the gasoline knocks badly in modern automotive engines. Lubricating oils are also produced from mixed-base oils, but acid treatment is usually necessary, and hence the expense of manufacture is greater. Vacuum distillation is particularly adapted to the processing of mixed- and naphthene-base oils because most of the asphalt or tarry material may be left as a distillation residue, and the distilled lubricating-oil stocks can be treated more easily than residual stocks. Naphthene-base oils produce good asphalt and usually in quantities large enough to justify its manufacture. The gasoline from naphthene crude oils is usually highly anti-knock and may often be sold directly as premium-grade motor fuel. Large quantities of residual fuel oil and gas oil, of mixed- and naphthene-base origin, are sold, but most of the residue that remains after skimming the gasoline and kerosene is cracked. By cracking, the total yield of gasoline may be increased from about 30 per cent by simple topping, to as much as 70 per cent by topping and cracking.



(a) TOPPING OR SKIMMING PROCESSING



(b) CRACKING PROCESSING



(c) LUBRICATING-OIL PROCESSING

Fig. 3.—Types of refinery processing.

The industry has adopted the following general types of processing:

Skimming or Topping Processing.—By simple distillation the crude oil is separated into gasoline, kerosene, fuel oil, or reduced crude oil and sometimes gas oil. Topping is practiced on all types of crude oils (Fig. 3*a*).

Cracking Processing.—This type of processing usually refers to a combined operation of skimming and cracking. No lubricating oils are produced in this type of operation. All bases of crude oil may be cracked, but the residual stocks from paraffin-base crude oils are seldom cracked (Fig. 3*b*).

Lubricating-oil Processing.—Skimming processing and the manufacture of lubricants are inferred by this type of processing, but no cracking is practiced. Paraffin-base crude oils are always processed for lubricants. Mixed-base oils are often processed thus, but naphthene oils are not processed for lubricants except under particularly favorable conditions (Fig. 3*c*).

Complete Processing.—Most of the larger plants practice skimming, cracking, and lubricant manufacture simultaneously, and this practice falls under the heading of complete processing.

The materials and methods outlined in this chapter constitute the most important ones. Many of the products found on the market are made by blending these stocks together to meet particular industrial requirements. As an example, the various grades of motor oil and machine oil are prepared by compounding different amounts and grades of the neutral oils and brightstock. Very heavy aero-oils, etc., consist mainly of brightstock, and sewing-machine oil consists mainly of nonviscous neutral oil. The details of the processing operations and the processing equipment will be enlarged upon in Chaps. XVII–XVIII.

CHAPTER IV

COMPOSITION OF PETROLEUM

Most of the compounds found in petroleum are composed of hydrogen and carbon. In addition to these materials, called hydrocarbons, other compounds containing small amounts of sulfur, oxygen, and nitrogen are also present. The physical operations of refining, such as vaporization, fractionation, and cooling, are governed to a large extent by the properties of the hydrocarbons because they constitute the bulk of the petroleum, but the chemical operations, such as treating and filtering, are governed by the presence of sulfur, oxygen, and nitrogen compounds and, to some extent, by the small amounts of reactive hydrocarbons that may be present. Russian crude oils[1] and certain naphthene-base oils contain relatively large amounts of oxygen. The oxygen is often combined in the form of naphthenic acids. Nitrogen is most often found in naphthene-base oils and is generally supposed to be in the form of basic compounds similar to the alkyl quinolines.[2] Sulfur may be present as dissolved free sulfur, hydrogen sulfide, or as organic compounds,[3] such as the thiophenes, sulfonic acids, mercaptans, alkyl sulfates, and alkyl sulfides. Some of these sulfur compounds are not found in crude petroleum, but they are produced from other compounds during distillation and refining. Only traces of sulfur have been found in typical paraffin-base oils. Sulfur compounds are particularly troublesome because they are usually foul smelling and some of them are corrosive.

Many series of hydrocarbons are found in crude petroleum, and still other series are produced by cracking and hydrogenation. Among the series that are said to have been identified in petroleum are those having the type formulae C_nH_{2n+2}, C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{2n-6}, C_nH_{2n-8}, C_nH_{2n-10}, C_nH_{2n-14}, and C_nH_{2n-20}. Inasmuch as most of the higher members of these series have never been produced synthetically or prepared in sufficient quantity for study, we have few compounds with which to compare those which are isolated from petroleum. Furthermore, the isolation of pure compounds is extremely difficult because the properties of adjacent members of a series differ from one another only slightly and because constant-boiling mixtures, which cannot be separated by fractionation, are prevalent. These difficulties and the multitude of hydrocarbons that are present in petroleum[4] have discouraged the study of petroleum chemistry.

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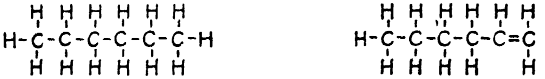
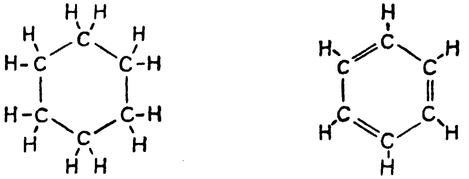
[1] VUISTAVKINA, T., *Neftyanoe Khozyaistvo*, **18,** 1000 (1930).

[2] SCHULZE, KING, and THOMPSON, *J. Am. Chem. Soc.*, **52,** 1239 (1930).

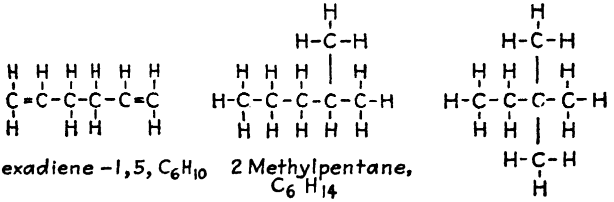
[3] EGLOFF and MORRELL, *Chem. Met. Eng.*, **28,** 633 (1923).



(a) Normal Hexane, C_6H_{14} (b) Normal Hexene, C_6H_{12}



(c) Cyclohexane, C_6H_{12} (d) Benzene, C_6H_6



(e) Hexadiene-1,5, C_6H_{10} 2 Methylpentane, C_6H_{14}

2-2 Dimethylbutane C_6H_{14}

(f) Isomeric Isoparaffin Compounds

FIG. 4.—Structural formulae of hydrocarbons.

Hydrocarbon Series.—Of the many hydrocarbon series present in petroleum, only a few have been studied thoroughly enough to guide commercial development. The best known series are the paraffin, olefin, naphthene, aromatic, diolefin, and acetylene (Figs. 4*a* to *f* are examples of the structural formulae of these types of compounds).

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[4] Some authorities estimate that 3,000 compounds may be present in crude petroleum.

The *paraffin series* (type formula C_nH_{2n+2}) is characterized by great stability. The name of each member ends in *-ane*—meth*ane*, eth*ane*, hex*ane*, and hexadec*ane*. At room temperatures the members, with the exception of those containing a tertiary carbon atom, are not acted upon by fuming sulfuric acid, concentrated alkalies, nitric acid, or even the powerful oxidizer chromic acid. They react slowly with chlorine in sunlight and with both chlorine and bromine if a catalyst is present.[5] Reaction usually occurs by the *substitution* of an element or a chemical group for a hydrogen atom. The lower members have been identified in most crude petroleums, but Mabery[6] reports that Mahoning County, Ohio, crude oil contains no paraffin hydrocarbons. The higher members of the paraffin series are probably present in most petroleums, although crude oils that are entirely free from wax may contain no high-boiling paraffin hydrocarbons. Paraffin wax probably consists of straight- or branched-chain paraffin hydrocarbons.[7] Egloff, Schaad, and Lowry[8] have made a thorough study of the decomposition of paraffin hydrocarbons (Fig. 4*a* and *f*).

The *olefin* or *ethylene series* (type formula C_nH_{2n}) is composed of unsaturated hydrocarbons; *i.e.*, the members of this series are capable of uniting directly with other materials such as chlorine, bromine, hydrochloric acid, and sulfuric acid, without displacing a hydrogen atom. The names of these hydrocarbons end in *-ene*, as eth*ene* (ethyl*ene*), prop*ene* (propyl*ene*), and but*ene* (butyl*ene*). Unsaturated compounds react with and dissolve in sulfuric acid and may thus be removed from petroleum oils. The low-boiling olefins are probably not present in crude petroleum, but they are found in cracked products. Egloff, Schaad, and Lowry[9] have made an excellent study of the literature of the olefin hydrocarbons (Fig. 4*b*).

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[5] Egloff, Schaad, and Lowry, The Halogenation of the Paraffin Hydrocarbons, *Chem. Rev.*, **8** (1) (1931).

[6] *Ind. Eng. Chem.*, **6**, 101–107 (1914).

[7] Buchler and Graves, The Petroleum Waxes, *Ind. Eng. Chem.*, **19**, 718 (1927).

[8] The Decomposition of the Paraffin Hydrocarbons, *J. Phys. Chem.*, **34**, 1617 (1930).

[9] The Decomposition and Polymerization of the Olefinic Hydrocarbons, *J. Phys. Chem.*, **35**, 1825 (1931).

The *naphthene series* (type formula C_nH_{2n}) has the same type formula as the olefin series but has greatly different properties. The naphthenes are ring or cyclic compounds, whereas the olefins are straight-chain compounds in which a double bond connects two carbon atoms. The naphthenes are saturated compounds and the olefins are unsaturated. Unsaturated compounds can react by direct combination with other materials, but saturated compounds can react only by the displacement of hydrogen by another material. In the older chemistry texts the naphthenes are called methylenes, *e.g.*, tetramethylene, pentamethylene, and hexamethylene, whereas the preferred names are now cyclobutane, cyclopentane, and cyclohexane. As an example of the relation of this series to other cyclic series, consider benzene and cyclohexane. Both compounds contain six carbon atoms per molecule, but six hydrogen atoms must be added to benzene to produce cyclohexane. The cyclohexane molecule is saturated, but the benzene molecule is highly unsaturated because it has three doubly combined carbon atoms (Fig. 4*d*). The three double bonds are active so that benzene is an active material, but the cyclohexane contains no double bonds and does not react readily. However, most of the reactions of benzene are by substitution rather than combination. The naphthenes, unlike their isomers the olefins, are not easily soluble in sulfuric acid. They have been found in almost all crude oils, but again Mahoning County crude oil is an exception.[6] This crude oil contained the hydrocarbons of the C_nH_{2n-2} and C_nH_{2n-4} series but no paraffins or simple naphthenes. Egloff, Bollman, and Levinson[10] have studied the reactions of the cyclo hydrocarbons (Fig. 4*c*).

The *aromatic series* (type formula C_nH_{2n-6}), often called the *benzene series*, is chemically active. These hydrocarbons are particularly susceptible to oxidation with the formation of organic acids. The aromatics may form either addition or substitution products, depending upon the conditions of the reaction. Only a few petroleums contain more than a trace of the low-boiling aromatics such as benzene and toluene. Mabery[11] found relatively large quantities of aromatics in Ventura, Coalinga, and Puente Hills, Calif., petroleums. Some of the Sumatra and

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[10] Thermal Reactions of Cycloparaffins and Cycloölefins, *J. Phys. Chem.*, **35**, 3489 (1931).

[11] *Proc. Am. Acad. Arts Sci.*, **36**, 255 (1901).

Borneo crude oils are rich in aromatics. This series is found in cracked distillates and is highly prized for its antiknock qualities (Fig. 4*d*).

The *diolefin series* (type formula C_nH_{2n-2}) is similar to the olefin series except that two hydrogen atoms are missing or two double bonds are present in each molecule. These double bonds cause the series to be extremely active. The diolefins tend to polymerize or combine with other unsaturated molecules forming high-molecular-weight gumlike solids. The diolefins and the gums from them are found in untreated cracked gasoline,[12] but they are probably not present in crude petroleum. They are polymerized and removed by sulfuric acid (Fig. 4*e*).

The *cyclic series* such as those having type formulae C_nH_{2n-2}, C_nH_{2n-4}, C_nH_{2n-8}, etc., are not well known. Nevertheless, the literature indicates that these series predominate in the higher boiling-point oils, such as gas oil and lubricating oils. Most of the hydrocarbons in lubricating oil are saturated, but Seyer[13] reports that about 20 per cent of a lubricating oil is soluble in sulfur dioxide. Doubtless the 20 per cent consists largely of unsaturated hydrocarbons.

Isomeric Compounds.—Confusion often arises because different compounds may have the same molecular formula. Isomeric compounds are those which have the same molecular formula but different internal structures. Compounds of the type formula C_nH_{2n} may be either saturated or unsaturated. The formulae of the saturated compound cyclohexane and the unsaturated compound hexene-1 may be compared in Fig. 4*b* and *c*. Likewise the formulae of *n*-hexane, 2-methyl pentane, and 2, 2-dimethyl butane, all having the type formula C_nH_{2n+2} or C_6H_{14}, may be compared in Fig. 4*a* and *f*. Groups of atoms such as the methyl groups in the compounds just referred to are called alkyl groups or radicals. These terms refer to a group of carbon and hydrogen atoms that may be conveniently considered as a unit because they usually act as a unit in a chemical reaction. They may be defined as a monovalent hydrocarbon radical having the general formula C_nH_{2n+1}. Common radicals are the methyl (CH_3), ethyl (C_2H_5), and propyl (C_3H_7) groups. Radicals are not individual compounds because they must always be attached to other radicals, elements, or groups of atoms.

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[12] BRIDGEMAN and ALDRICH, *Oil Gas J.*, Jan. 29, 1931, p. 42.

[13] *Petroleum Equipment Exporter*, January, 1930, p. 65.

There are two possible isomeric butanes, *viz.*, *n*-butane and 2-methyl propane; three pentanes; five hexanes; and nine heptanes. The number of possible isomeric hydrocarbons increases rapidly as the number of carbon atoms increases. Compounds of the type formula C_nH_{2n-4} present even more possibilities of isomerism than the foregoing. As an example, the saturated series might consist of three doubly combined rings or combined rings with alkyl side-chains; the unsaturated series might consist of numerous compounds having unsaturated carbon atoms in the rings, in the side-chains, or in both; and other series might exist having combinations of saturated or unsaturated rings with saturated, unsaturated, or acetylene side-chains. Consideration of the series that are even more deficient in hydrogen than the C_nH_{2n-4} series indicates that an enormous number of isomers is possible. Fortunately the number of unsaturated, high-molecular-weight hydrocarbons in petroleum are probably few, or the isolation of these complex compounds would prove an endless task.

Determination of Series.—Although chemists have not yet determined procedures and reagents for the isolation of each chemical series, a start toward this goal has been made.[14] The proposed methods do not indicate the exact series of hydrocarbons that are present, but they do indicate groups of compounds that behave chemically as the paraffin, olefin, aromatic, or naphthene series. All double-bonded hydrocarbons such as the olefins, diolefins, and double-bonded cyclics are classed together as one group, called unsaturates. The unsaturated group may be absorbed or polymerized by sulfuric acid; the aromatics may be nitrated or absorbed by fuming sulfuric acid or dissolved by dimethyl sulfate; the naphthenes may be determined by means of the aniline index; and the paraffins are found by difference. Such an analysis is perhaps just as valuable to the engineer as an exact one, because he is concerned with the retention or elimination of certain properties in the finished products rather than with a detailed knowledge of exactly what compounds are present. By means of the foregoing analysis of chemical properties and the physical constants of each series, a reliable estimate or check of the physical constants for any petroleum oil is possible. Such an analysis, to be of most value, should be made on each of, say, 10 fractions of a crude oil, so that the change in the percentage of each series can be followed throughout the entire boiling-range of the oil. One of the first studies of this kind was made by Robinson,[15] and the results of his study have been presented in graphical form in "Motor Fuels," by E. H. Leslie.[16]

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[14] EGLOFF and MORRELL, *Ind. Eng. Chem.*, **18**, 354 (1926).

Composition of Petroleum.—In the past, petroleum has often been considered as a solution of the paraffin hydrocarbons, but a survey of the literature indicates that such an assumption is not justified. The paraffins predominate in most gasolines[13,14] and probably in kerosenes from paraffin- and mixed-base petroleum; the naphthenes predominate in most gas oils and lubricating oils from all bases of crude oils; and the naphthenes, aromatics, and unsaturated hydrocarbons constitute the bulk of the highest boiling or residual products. The only paraffins present in the higher boiling products appear to be those occurring in the wax, and the amount of wax in even paraffin-base petroleum is relatively small. Sachanen and Wirabian[17] present analyses of several Russian and American oils (Table 1).

TABLE 1.—CHEMICAL ANALYSES OF PETROLEUM, PER CENT

Fraction, deg. F.	1. Grozny ("high paraffin"), 45.3 per cent at 572°F.			2. Grozny ("paraffin-free upper level") 40.9 per cent at 572°F.			3. Oklahoma (Davenport), 64 per cent at 572°F.			4. California (Huntington Beach), 34.2 per cent at 572°F.		
	Aromatic	Naphthene	Paraffin	Aromatic	Naphthene	Paraffin	Aromatic	Naphthene	Paraffin	Aromatic	Naphthene	Paraffin
140-203	3	25	72	4	31	65	5	21	73	4	31	65
203-252	5	30	65	8	40	52	7	28	65	6	48	46
252-302	9	35	56	13	52	35	12	33	55	11	64	25
302-392	14	29	57	21	55	24	16	29	55	17	61	22
392-482	18	23	59	26	63	11	17	31	52	25	45	30
482-572	17	22	61	35	57	8	17	32	51	29	40	31

Table 2 shows a similar study of the composition of gasoline. Table 3 indicates in a general way the series of hydrocarbons that have been found in the Pennsylvania, Mid-Continent, and

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[15] *Chem. Met. Eng.*, **11**, 389–394 (1913).

[16] Chemical Catalog Company, Inc., New York, 1923.

[17] *Petroleum Z.*, **25**, 867 (1929).

TABLE 2.—CHEMICAL ANALYSES OF GASOLINE*

Gasoline	Unsaturated	Aromatic	Naphthenic	Paraffinic
1. Cracked from Kentucky fuel oil	14.4	22.5	10.0	53.1
2. Cracked from Smackover fuel oil	14.7	27.5	21.2	36.6
3. Cracked from North Texas fuel oil	16.0	18.6	11.7	53.7
4. Cracked from Lost Soldier, Wyo	11.7	15.0	15.4	57.9
5. Cracked from Cushing, Okla	10.9	19.8	18.0	51.3
6. Cracked from Somerset, Ky	12.5	14.9	11.8	60.8
7. Straight-run from Cushing, Okla	1.6	4.9	23.7	69.8
8. Straight-run from Somerset, Ky	3.8	5.3	20.6	70.3
9. Commercial	4.5	12.1	17.6	65.8
10. Houdry from M.C. and Gulf Coast gas oil, 437°F. cut	8.0	24.0	21.0	47.0
11. Houdry from Coastal crude, 437°F. cut	24.0	18.0	24.0	34.0

* Egloff (except 10 and 11, from Catalytic Development Company).

TABLE 3.—HYDROCARBON SERIES FOUND IN PETROLEUM

No. of carbon atoms	Pennsylvania	Mid-Continent	California and Gulf Coast
5	C_nH_{2n+2}	C_nH_{2n+2}	C_nH_{2n} and C_nH_{2n+2}
10	C_nH_{2n+2}	C_nH_{2n+2} and C_nH_{2n}	C_nH_{2n} and C_nH_{2n-6}
15	C_nH_{2n+2}	C_nH_{2n-2}	C_nH_{2n-2}
20	C_nH_{2n}	C_nH_{2n-4}	C_nH_{2n-4}
25	C_nH_{2n} and C_nH_{2n-2}	C_nH_{2n-4}	C_nH_{2n-4}
30	C_nH_{2n} and C_nH_{2n-4}	C_nH_{2n-8}	C_nH_{2n-8}
35	C_nH_{2n-4} and C_nH_{2n-8}	C_nH_{2n-8} and C_nH_{2n-12}	C_nH_{2n-12}
40	C_nH_{2n-4} and C_nH_{2n-8}	C_nH_{2n-8} and C_nH_{2n-12}	C_nH_{2n-12} and C_nH_{2n-16}
50	C_nH_{2n-8}	C_nH_{2n-8} and C_nH_{2n-12}	C_nH_{2n-16}
80	C_nH_{2n-8}	C_nH_{2n-16}	C_nH_{2n-20}

California oils. The C_nH_{2n-8}, C_nH_{2n-12}, C_nH_{2n-16}, and C_nH_{2n-20} series were taken from Mabery's study of lubricant and asphaltic hydrocarbons.[18]

The ultimate composition[19] of a few petroleums is listed in Table 4.

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[18] *Ind. Eng. Chem.*, **15**, 1233 (1923).

[19] Int. Crit. Tables, **II**, 136–162 (1927).

TABLE 4.—ULTIMATE CHEMICAL ANALYSES OF PETROLEUM

Petroleum	Sp. gr.	At °C.	Per cent C	Per cent H	Per cent N	Per cent O	Per cent S	Base
Pennsylvania pipe line	0.862	15	85.5	14.2	....	...	....	Paraffin
Mecook, W. Va	0.897	0	83.6	12.9	3.6			Paraffin
Humbolt, Kans	0.912	..	85.6	12.4	....	...	0.37	Mixed
Healdton, Okla	.....	..	85.0	12.9	....	...	0.76	Mixed
Coalinga, Calif	0.951	15	86.4	11.7	1.14	...	0.60	Naphthene
Beaumont, Tex	0.91	..	85.7	11.0	2.61		0.70	Naphthene
Mexico	0.97	15	83.0	11.0	1.7		4.30	Naphthene
Baku, U.S.S.R	0.897	..	86.5	12.0	....	1.5		
Colombia, South America	0.948	20	85.62	11.91	0.54			

Vapor-pressure.—One of the most useful physical properties is the vapor-pressure-temperature-relation. The vapor-pressure of a liquid is a measure of the tendency of the liquid to vaporize. Thus the vapor-pressure is involved in problems of condensation, vaporization, fractionation, and the correction of boiling-points from one pressure to another. Figure 5 is a chart of the vapor-pressures of the normal paraffin hydrocarbons (horizontal lines) and of a few other compounds (sloping lines). The data for the paraffin hydrocarbons and the convenient form of chart were developed by Dr. G. G. Brown[20] of the University of Michigan. The acetylene and olefin curves were taken from Rechenberg's "Einfache und fractionierte Destillation," and the curves for the other hydrocarbons from the International Critical Tables. The curves for all of the compounds except the paraffins and acetylenes slope downward to the right, and the few data that are available concerning petroleum fractions indicate the same tendency.

Example 1. Use of Vapor-pressure Chart.—What is the vapor-pressure of *n*-butane at 77°F. (25°C.)?

Twenty-five degrees centigrade is located among the vertical lines. The vapor-pressure of butane is found as a horizontal line. These two lines intersect on the 1,800-mm. pressure-line. The vapor-pressure is 1,800 mm.

What is the boiling-point of butane at atmospheric pressure?

Follow the butane line until it crosses the 760-mm. line. Reading directly below this point, the temperature is 0°C.

Compression Factor.—When gases or vapors are compressed or expanded under adiabatic conditions, the amount of work done

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[20] *Proc. 7th Ann. Convention Nat. Gaso. Assoc. America*, **1928.**

TABLE 5.—COMPRESSION FACTORS

Gas	Temperature, deg. F.	$\gamma = C_p/C_v$	Pressure, atm.
Methane	−175	1.41	1
Methane	−112	1.34	1
Methane	−101	1.35	1
Methane	32	1.307	1
Methane	212	1.232	1
Methane	392	1.188	1
Methane	572	1.16	1
Methane	752	1.139	1
Ethane	−115	1.28	1
Ethane	59	1.22	1
Ethane	122	1.21	1
Ethane	212	1.19	1
Ethene (ethylene)	132	1.35	1
Ethene	212	1.18	1
Ethine (acetylene)	− 96	1.31	1
Propane	61	1.13	0.5
Isobutane	59	1.11	1
Pentane	187	1.08	1
Hexene	176	1.08	1
Hexane	176	1.08	1
Benzene	194	1.1	1

and the amount of heat required are dependent upon the ratio of the specific heat at constant pressure to the specific heat at constant volume. The expansion of a gas can always be expressed by an equation of the form

$$P_1V_1^n = P_2V_2^n = \text{a constant}$$

At adiabatic conditions the exponent n is referred to as gamma (γ) and is equal to the ratio of the specific heats as mentioned above. Table 5 is a list of the values of gamma for some of the more common gaseous hydrocarbons. The value of gamma decreases at higher temperatures and also for high-molecular-weight materials. For hydrocarbons such as those in kerosene and heavier oils, the value of gamma approaches unity, and hence only a small refrigeration effect is noted when these vapors are expanded adiabatically. W. C. Edmister[21] presents a chart by which the value of gamma may be computed over wide ranges of temperature and pressure.

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[21] Specific Heat Ratios for Hydrocarbons, *Ind. Eng. Chem.*, **32**, 373 (1940).

Detonation Characteristics.—The methods of determining the octane number or detonation characteristics of a motor fuel have been changed so frequently that octane numbers of the various hydrocarbons by the newest methods are not available. However, the relation between the detonation characteristics and the internal structure of many petroleum hydrocarbons has been given careful study. Lovell, Campbell, and Boyd[22] of the General Motors Corporation have presented several valuable

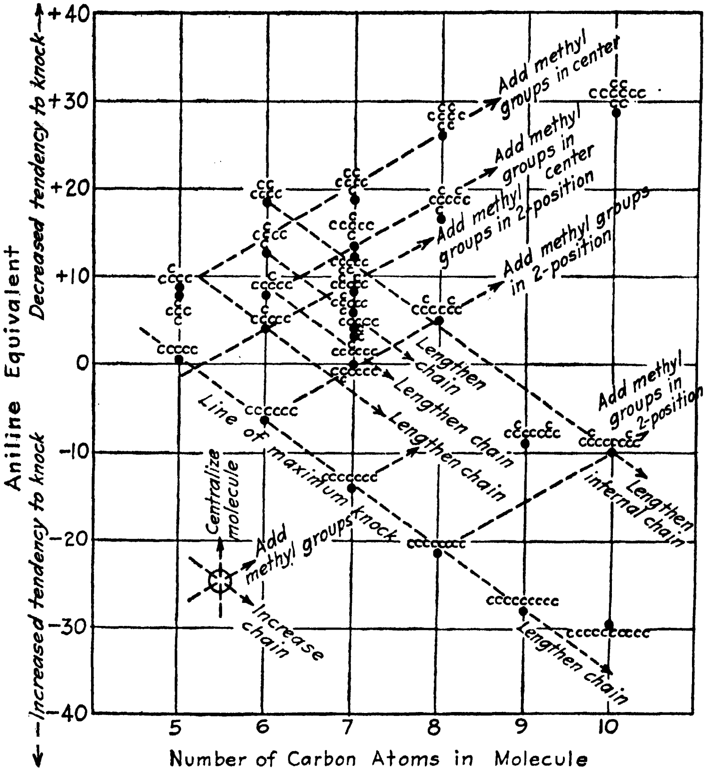

FIG. 6.—Detonation characteristics of the paraffin hydrocarbons. (*General Motors Corporation.*)

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[22] Paraffins, *Ind. Eng. Chem.*, **23**, 26 (1931); Olefins, **23**, 555 (1931); Naphthenes, **25**, 1107 (1933).

papers concerning antiknock characteristics. Figure 6 summarizes their findings for the paraffin hydrocarbons. The relative knocking tendency is compared by means of the aniline equivalent. Positive aniline equivalents indicate compounds that knock less than the reference fuel (zero aniline equivalent), and negative equivalents indicate materials that knock more than the

	Octane No. by motor method*		Octane No. by motor method*
Paraffin hydrocarbons:		2,4,4-Trimethyl pentene-2	89 (133)
Butane	91	3,4,4-Trimethyl pentene-2	85.6 (72.5)
2-Methyl propane	99	2-Methyl octene-1	74.8 (69.8)
Pentane	64	3-Methyl octene-1	83.5 (72.2)
2-Methyl butane	90 (81)	3-Methyl octene-2	84
2,2-Dimethyl propane	83	2,6,6-Trimethyl heptene-2	73.6 (70.0)
Hexane	59	Di-isoamylene	75
2-Methyl pentane	73	Tri-isobutylene	87
3-Methyl pentane	74.5	Naphthene hydrocarbons:	
2,2-Dimethyl butane	95	Ethyl cyclobutane	— (68)
2,3-Dimethyl butane	95	Cyclopentane	— (116)
Heptane	0	Methyl cyclopentane	82
2-Methyl hexane	64	Cyclohexane	87 (81)
2,2-Dimethyl pentane	93	Methyl cyclohexane	71 (81)
2,3-Dimethyl pentane	85	1,2-Dimethyl cyclohexane	— (62)
2,4-Dimethyl pentane	90	1,4-Dimethyl cyclohexane	— (67.5)
3,3-Dimethyl pentane	83.5	Ethyl cyclohexane	— (57.5)
2,2,3-Trimethyl butane	101	1-Methyl, 2 Ethyl cyclohexane	— (55)
Octane	−28		
3-Methyl heptane	34.5	1-Methyl, 2 Propyl cyclohexane	— (71)
2,3-Dimethyl hexane	75.5		
2,5-Dimethyl hexane	52	1-Methyl, 2 Butyl cyclohexane	— (87)
3,4-Dimethyl hexane	84.5		
2,2,3-Trimethyl pentane	100.2	Aromatic hydrocarbons:	
2,2,4-Trimethyl pentane	100	Benzene	97 (87)
2,2,3,3-Tetramethyl butane	103	Toluene	100+ (90)
3-Methyl,3-Ethyl pentane	90.5	*o*-Xylene	100+ (97)
Nonane	−28	*m*-Xylene	100+ (104)
2-Methyl octane	98 (70.3)	*p*-Xylene	100+ (104)
3-Methyl octane	94 (65.7)	Ethyl benzene	96 (97)
2-Methyl nonane	93	1,3,5-Trimethyl benzene	— (109)
2,2,6-Trimethyl heptane	94.8 (69.0)	Isopropyl benzene	— (87)
Olefin hydrocarbons:		1,3-Diethyl benzene	— (126)
Butene-1	80	Butyl benzene	— (82)
Butene-2	83	Sec. Butyl benzene	— (78)
2-Methyl propene	87	Tert. Butyl benzene	— (88)
2-Methyl hexene-1	75	Other hydrocarbons:	
2-Methyl hexene-2	84	Butadiene-1,3	— (83.5)
2,4,4-Trimethyl pentene-1	86	Cyclohexene	— (97)

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* More complete listings for octane numbers by the research method are given in the same reference.

reference fuel. For the paraffin hydrocarbons the tendency to knock is decreased by

1. Shortening the main chain.
2. Introducing side-chain groups such as methyl groups.
3. Centralizing the molecule by adding methyl groups about the center of the main chain.

The tendency of the olefin hydrocarbons to knock is decreased by

1. The same three factors as for the paraffin hydrocarbons.
2. Moving the double bond toward the center of the chain.

The tendency of the naphthenes to knock is decreased by

1. Decreasing the size of the ring.
2. Decreasing the length of the longest unbranched side-chain.
3. Distributing the carbon atoms in the side-chains into many short chains rather than one long chain.
4. Centralization of the side-chains.

These general relationships are apparent in the tabulation of octane numbers shown in the table on page 32, taken from the excellent "Physical Constants of the Principal Hydrocarbons" compiled by the Technical and Research Division of the Texas Company, 1939. The equivalent octane number when used in blends is shown in parenthesis.

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CHAPTER V

ROUTINE LABORATORY TESTS

A discussion of the large number of routine tests that are practiced today could easily fill an entire book. These tests were developed to provide simple methods of comparing products during their manufacture and as they appear on the business market. Although many companies have developed their own test methods, certain tests have been accepted as standards. In this chapter emphasis will be placed on the engineering importance of these tests rather than upon the details of laboratory procedure. Those who are interested in laboratory manipulations may refer to the references at the end of the chapter and particularly to Petroleum Products and Lubricants,[1] a report by Committee D-2 of the American Society for Testing Materials (A.S.T.M.).

Routine or control tests are not satisfactory unless they can be (1) performed quickly, (2) easily duplicated by ordinary laboratory men, and (3) interpreted as a function of the performance of the material while in use. For these reasons routine tests may not be scientifically exact, but they are more valuable for general use than more elaborate tests would be. The procedures for such tests must be carefully specified and rigidly adhered to, or the results will not be dependable. Because of the empirical nature of most routine tests, the results become intelligible only by comparison with a large number of similar tests and by a careful correlation with the performance of the product.

As an example, the A.S.T.M. distillation must be conducted in a flask having specified dimensions; the rate of heat input must be regulated so that the first drop of distillate is collected at a particular time and the rate of distillation thereafter is uniform; a special thermometer must be used; and the condenser must be held at a specified temperature. Even slight variations in the procedure, such as excessive drafts of air or an erratic rate of distillation, will cause erroneous results. If the procedure of the test is carefully followed, the resulting distillation curve can be duplicated by other laboratories and will be a useful indication of the properties of the sample. However, in spite of the reliability of the test and its great value to the industry, it is not a true measure of the composition of the sample. The sample will contain material that boils below the initial boiling-point (I.B.P.), as recorded in the A.S.T.M. distillation, and will contain material that boils at a higher temperature than the end-point (E.P.) of the A.S.T.M. distillation.

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[1] *Report of Committee* D-2, A.S.T.M., Philadelphia, yearly.

Many articles have been published in which the A.S.T.M. distillation has been correlated with the performance of a motor fuel in an engine. The temperature at which various percentages of a motor fuel will distill has been found to bear a relation to the ease of starting, acceleration, losses of fuel, and vapor-lock tendencies of the fuel.

All of the design data that an engineer needs cannot be obtained from routine tests, and to obtain complete design data he must resort to special methods such as those outlined in Chaps. VI and VII. Nevertheless, routine tests are the common basis of understanding between the refiner and the business world. The engineer, although he may not use routine tests in design, must produce products that are ultimately compared with other commercial products by routine tests.

Refinery Control.—Routine tests are universally used as the basis for controlling refinery operations. During the first few months of the operation of a new equipment many of the products are tested at 2-hr. intervals. Soon certain of these tests begin to assume importance as criterions of the operation, and by these tests the unit is controlled throughout its useful life. Products are periodically tested throughout the whole refinery. Not only are the raw materials and finished products examined but also the materials that are in the process of being finished. The finished products are often examined a second time after they have been loaded into cars and containers for the market. In filling such an extensive need, it is clear that routine tests must be simple and dependable.

A.P.I. and Specific Gravity.—The specific gravity and the A.P.I. (American Petroleum Institute) gravity are expressions of the density or the weight of a unit of material. The specific gravity is the ratio of the weight of a unit volume of oil to the weight of the same volume of water at a standard temperature. The specific gravity of an oil is always given at 60°F. referred to water at 60°F. Unless otherwise stated, both the specific gravity and A.P.I. gravity refer to these constants at 60°F. In plant practice the A.P.I. gravity is usually used. This scale is not directly related to the specific gravity. If the modulus of the A.P.I. is used, the relation between the specific gravity and the A.P.I. gravity is (also see tabulation in Appendix):

$$\text{Deg. A.P.I.} = \frac{141.5}{\text{sp. gr.}} - 131.5 \qquad (1)$$

or

$$\text{Sp. gr.} = \frac{141.5}{\text{A.P.I.} + 131.5}$$

The Baumé scale of gravity, which was previously used in the industry, is slightly different from the A.P.I. gravity. The constants in the foregoing equation are 140 and 130 rather than 141.5 and 131.5.

The specific gravity[1] (D287-39) or A.P.I. gravity is measured in the laboratory by means of hydrometers or the chainomatic specific-gravity balance. The latter is desirable if a large number of exact determinations must be made or if very small samples (15 cc.) must be used. For viscous oils or semi-solid bitumens the pycnometer[1] (D70-27) or weighing bottle is used, and for solid materials an analytical balance[1] (D71-27), equipped with a pan straddle, may be employed.

In the past Appalachian petroleums were the only widely known oils, and the specific gravity was an important specification because it was directly related to other properties of the oil. Today, with the development of a large variety of crude oils, the specific gravity is much less important. However, the specific gravity does indicate the approximate boiling-range of an oil and to some extent the base of oil from which the product was produced. There is a relation between the gravity of a raw oil and the base of the oil, but the gravity is influenced by chemical treatment and by the boiling-range of the material.

A.S.T.M. Distillation.—In determining the boiling-range of gasoline and kerosene, the procedure and apparatus, as described in the Report of Committee D-2[1] (D86-38 and D216-39), is used. The name A.S.T.M. distillation is used because the method was first standardized by the American Society for Testing Materials. A somewhat similar test known as the "Engler distillation" has been used in the past, and often the A.S.T.M. distillation is referred to as "an Engler."

One hundred cubic centimeters of oil is distilled at a uniform rate of 5 cc. per minute. The distillate is condensed in a brass tube surrounded by cracked ice. The temperature of the vapor when the first drop of condensate drips from the condenser (in not less than 5 or more than 10 min.) is recorded as the "initial boiling-point." The vapor temperature is also recorded as each successive 10 per cent is collected. When 95 per cent has been distilled, the burner flame may need to be increased, and the maximum temperature is recorded as the "end-point."

Virtually no fractionation occurs in this distillation, and the hydrocarbons in the oil do not distill one by one in the order of their boiling-points but as successively higher and higher boiling mixtures. The details of this inadequacy will be discussed under vaporization in Chap. XIV. Actually, the initial boiling-point, the end-point, and the intermediate vapor-temperatures have little significance except when compared with corresponding points from other A.S.T.M. distillations. Material boiling below the initial boiling-point and above the end-point are present in the oil, although these points are the extreme ends of the A.S.T.M. distillation range. In routine plant reports the loss is plotted at the end of the distillation curve, but for more scientific work it is usually plotted at the beginning of the curve. A comparison between the A.S.T.M. distillation and a true-boiling-point (T.B.P.) distillation is given in Figs. 68, 69 and 81 (pages 225 and 253).

Flash- and Fire-points.—The flash-point and the fire-point are further indications of the range and nature of the boiling-point curve. They designate respectively the temperature at which the vapor above an oil will momentarily flash or explode when in the presence of a flame and the temperature at which the vapors are evolved rapidly enough to burn continuously. These tests serve to indicate the temperature below which an oil can be handled without danger of fire. Certain high-boiling oils, such as lubricants, cannot be distilled at atmospheric pressure without thermal decomposition, and in such a case the flash-point helps to indicate the relative amount of low-boiling oil present in the material.

The common flash-point instruments are the *open cup*[1] (D92-33) and *Pensky-Martens*[1] (D93-36) closed tester for heavy oils and the *Tag*[1] (D56-36) closed tester for light oils. The oil is heated at the rate of 10°F. per minute in the heavy oil testers and at 1.8°F. in the Tag tester. A test flame is introduced into the vapor at 30-sec. intervals. The flash-point by the Martens tester is about 10° lower than by the open tester; but if the flash-point is above 510°F. (Martens), a larger difference exists between flash-points by the two instruments. The closed instrument is the more exact of the two, but the open cup is used extensively because of its simplicity. The flash- and fire-points are important specifications of kerosene, fuel oil, and lubricating oil.

Color.—The color of an oil serves as an indication of the thoroughness of the refining process. True, oils of different boiling-range and from different crude oils may have different colors; but other things being comparable, the color indicates the degree of refining that the material has undergone. Distilled products that are discolored are an indication of (1) thermal decomposition, (2) the entrainment of dark-colored tarry material, or (3) materials that are inherently dark in color. Discoloration by decomposition is due to the use of too high temperatures, and discoloration by entrainment is usually due to "throughputs" above the maximum capacity of the equipment. The success of a chemical treating operation is often measured by the improvement in color.

The *Saybolt chromometer*[1] (D156-38) is used to determine the color of gasoline and burning-oils, and the *Union colorimeter*[1] (D155-39T) for lubricating oils. Both of these instruments have empirical color scales which bear no direct relation to the Lovibond color analysis. For lubricating oil colors the *Tag Robinson* color instrument is also finding favor. The Saybolt chromometer color scale ranges from 30 for fine gasoline to 15 for mineral-seal burning-oil. Normally, one or two color disks are used, but a so-called "half-disk" is available for colors from +25 to +30. If the half-disk is used, the heights and colors are

Height, In.	Color
20	30
18	29
16	28
14	27
12	26

The A.S.T.M. color numbers are used almost universally in stating the color of lubricating oils. Table 6 presents a comparison of the A.S.T.M. numbers, the Lovibond colors (No. 500 series), and the National Petroleum Association or Union colorimeter letters.

TABLE 6.—COMPARISON OF COLOR SCALES

N.P.A. names	A.S.T.M. numbers	Union Petroleum Company letters	Lovibond color	Cell length, in.
1. Lily white	1	G	11	6
2. Cream white	1½	H	26	6
3. Extra pale	2	I	98	6
4. Extra lemon pale	2½	J	193	6
5. Lemon pale	3	K	290	6
6. Extra orange pale	3½	L	380	6
7. Orange pale	4	M	525	6
8. Pale	4½	N	65	½
9. Light red	5	O	80	½
10. Dark red	6	P	110	½
11. Claret red	7	Q	165	½
12.	8	R	205	½
13. Cylinder oil, extra light (filtered)	A	A	35	½
14. Cylinder oil, light (filtered)	D	D	70	½
15. Cylinder oil, medium (filtered)	E	E	170	½

Viscosity.—The viscosity of an oil is a measure of its resistance to internal flow and is an indication of its oiliness in the lubrication of surfaces. In the centimeter-gram-second (c.g.s.) system the unit of viscosity is the poise or centipoise (0.01 poise). Viscosity may be defined as the force in dynes required to move a plane of 1 sq. cm. area, at a distance of 1 cm. from another plane of 1 sq. cm. area, through a distance of 1 cm. in 1 sec.

The *relative viscosity* is the ratio of the viscosity of the liquid to that of water at 69.33°F. The viscosity of water at 69.33°F. is

1 centipoise, and hence the relative viscosity and the viscosity in centipoises are numerically equal. Two other common terms are *kinematic viscosity*, which is the viscosity in centipoises divided by the specific gravity at the same temperature, and *fluidity*, which is the reciprocal of viscosity. The units of kinematic viscosity are stokes and centistokes.

The common viscosimeters do not read directly in centipoises. All employ arbitrary scales of viscosity. The *Saybolt Universal viscosity*[1] (D88-38) is the time, measured in seconds, required for the efflux of 60 cc. of oil from a container tube at a constant temperature through a calibrated orifice in the bottom of the tube. In the United States the usual temperatures for the measurement of viscosity are 70, 100, 122, 130, and 210°F. The procedure in determining the viscosity involves straining the oil to remove particles that might lodge in the orifice, bringing the oil to a constant temperature by means of a constant-temperature bath, and accurately measuring the time for efflux. The *Saybolt Furol viscosity*[1] (D88-38) is determined exactly as is the Universal viscosity except that a larger orifice is used. Both of these viscosities are determined with the same instrument, the Universal viscosimeter.[1] The viscosity of lubricants is usually reported as Saybolt Universal seconds at 100, 130, or 210°F., and of fuel oils as Saybolt Furol seconds at 122 or 210°F.

Kinematic viscosity may be determined directly by means of Ubbelohde, FitzSimmons modification or modified Ostwald viscosimeter pipettes[1] (D445-39T). A series of these pipettes which cover the entire useful range of viscosity may be suspended in a single constant-temperature bath. Great accuracy is possible with these instruments, and a somewhat smaller sample is satisfactory, but each instrument must be calibrated.

If t is the Saybolt Universal viscosity and z and s respectively are the viscosity in centipoises and the specific gravity, all three factors taken at the same temperature, the relation among these variables, according to the Bureau of Standards, is

$$\text{Kinematic viscosity} = \frac{z}{s} = 0.219t - \frac{149.7}{t} \qquad (2)$$

The A.S.T.M. recommends a series of conversion factors[1] (D446-39) by which centistokes can be converted into Saybolt Universal viscosity.

The viscosity of gasoline and kerosene cannot be determined in the Saybolt viscosimeter because the large orifices result in turbulent rather than streamline flow. The viscosity of such liquids is determined in the Saybolt *Thermoviscosimeter*.[2] The

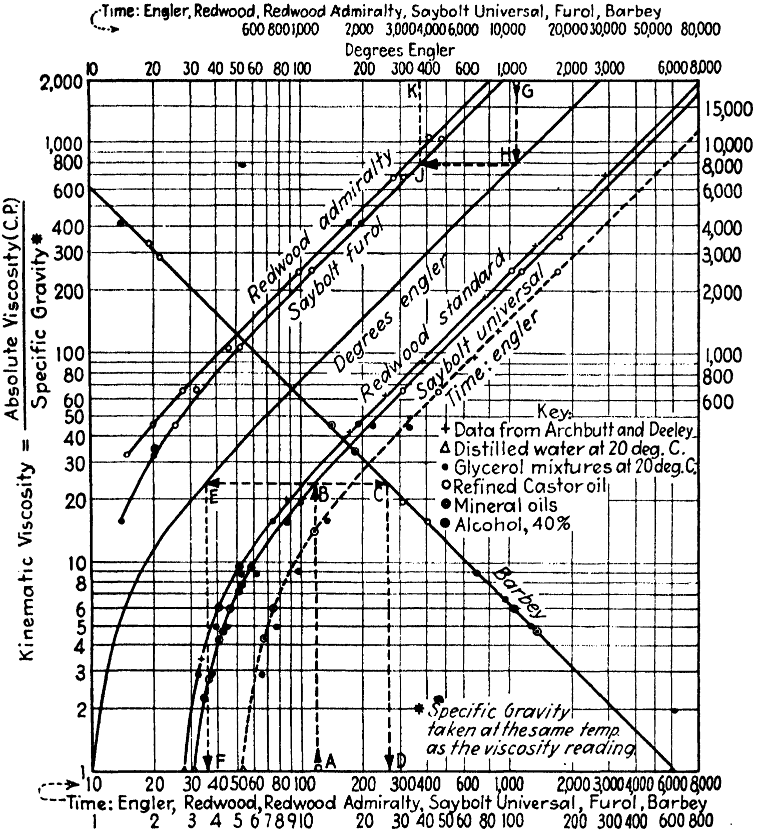

FIG. 7.—Comparison of viscosity by different instruments. (*The Texas Company.*)

thermoviscosity of kerosene is sometimes specified because kerosene must be readily absorbed in a lamp wick. Figure 7[3] may be used to convert the viscosity by any one of the viscosimeters to the viscosity by any of the other common instruments.

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[2] BENNETT, H. T., *Petroleum Age*, Dec. 15, 1921.

[3] *Lubrication*, May, 1921, published by the Texas Company.

Although Fig. 7 is useful for approximating the viscosity for design work or estimates, it should not be used for exact specifications. If the viscosity of a shipment of oil is specified in particular units, the viscosity should be determined in these units by using the proper instrument.

Example 2. Use of Viscosity Conversion Chart (Fig. 7).—The Saybolt viscosity is 1,000 sec. at 210°F. What is the Furol viscosity at 210°F.?

Trace the 1,000 time line to the intersection with the Saybolt Universal line. Follow the horizontal line (kinetic viscosity of approximately 215.0) to the Saybolt Furol line. Read down from the intersection. The Saybolt Furol time at 210°F. is approximately 103 sec.

The Engler time corresponding to the foregoing is 1,500 sec. The Engler degrees (or number) corresponding to the foregoing is 30.

The lower and left scales are used for Saybolt Universal viscosities up to 8,000. For higher viscosities the upper and right scales are used.

Cloud- and Pour-points.—The cloud- and pour-points are useful in estimating the relative amount of wax in an oil. However, all oils will solidify if cooled to a low enough temperature, and hence these tests do not indicate the actual amount of wax or solid material in the oil. They do indicate that most of the wax, melting above the pour-point, has been removed.

In the *cloud test*[1] (D97-39) the oil is cooled, from at least 25°F. above the cloud-point, in a specified test jar. The cooling bath is held between 15 and 30°F. below the cloud-point of the oil. At intervals the test jar is removed from the brine bath without disturbance to the oil, and the temperature at which a distinct cloudiness or haziness appears in the bottom of the jar is recorded as the cloud-point. The *pour test*[1] (D97-39) is conducted in much the same manner. However, the oil is first heated to 115°F., to be sure that all wax has dissolved, and cooled to 90°F. before the test. As in the cloud test the bath is held 15 to 30°F. below the estimated pour-point. At intervals of 5° the test jar is removed from the bath and tilted to ascertain if the oil will flow or move. If it shows no movement when the jar is held horizontal for 5 sec., it is said to be solid. The pour-point is taken as the temperature 5°F. above the solid-point.

The term *cold test* is used loosely and may refer to either the cloud or the pour test. Much confusion can be avoided if the proper term cloud test or pour test is used. Years ago the industry had a specified cold test which indicated the capacity of the oil to flow after vigorous stirring at a low temperature. This test proved to be inadequate and should not be confused with the cloud or pour tests of today.

These tests are for the purpose of ascertaining if an oil will function properly as a lubricant at low temperatures. Since 1929 effective methods for the removal of wax have been developed, and the average specified pour-point for lubricating oils has been lowered from 30 to about 0°F.

Knock Characteristics.—The confusion that has long characterized the methods of testing the knock characteristics of motor fuels does not appear to have abated.[4] *Normal heptane* and 2,2,4-*trimethyl pentane* (so-called isooctane) have been adopted as measuring sticks of knock intensity, and a standard engine known as the *C.F.R.* (Cooperative Fuel Research) *engine* has been adopted. The unit of knock intensity known as *octane number* is defined as the percentage by volume of isooctane that must be mixed with normal heptane in order to match the knock intensity of the fuel that is undergoing test. Since these hydrocarbons are expensive, reference gasolines that have been standardized against octane-heptane mixtures are used in commercial work.

Several sets of operating conditions have been employed such as those known as the research method, the motor method[1] (A.S.T.M. D357-39), the L-3 method, and finally a 1939 research method.[4] In the face of such changes in method, details of the procedure at any one time are of little value. In general, however, the research methods utilize an engine speed of 600 r.p.m., and the other methods, a speed of 900 r.p.m.; the jacket temperature is 212°F.: and the main controversy concerns the mixture temperature and spark advance.

Sulfur Tests.—The sulfur[1] (D90-34T) content of gasoline and burning-oils is an important specification. Sulfur causes many corrosion difficulties. Twenty cubic centimeters of oil is burned in a small lamp, and the products of combustion are drawn through a sodium carbonate absorption solution. The sulfur is determined by titrating the unused sodium carbonate solution. Sulfur in residual fuel oil and crude oil is determined by the ordinary oxygen-bomb method[1] (D129-39).

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[4] The author has always contended that tests should bear some close connection with road performance, but in this instance the wide variety of fuels, cars, and conditions under which they must operate may make it impossible to develop a laboratory test that is satisfactory in this respect. Certainly the vacillation from test method to test method under what may be the concerted action of groups selfishly advising changing of the test to favor cracked gasolines, leaded gasolines, or catalytic gasolines, etc., is not conducive to sound development.

The presence of corrosive materials such as free-sulfur and corrosive sulfur compounds is always objectionable. The test[1] (D130-30) consists in noting the effect of the heated oil on a strip of polished copper. More than a slight discoloration of the copper after heating for 3 hr. indicates that the oil is corrosive.

Tests for Bituminous and Semi-solid Materials.—The most common tests for asphaltic substances are the ductility, penetration, softening-point[1] (D36-26), and specific-gravity tests. The *ductility*[1] (D113-39) of an asphalt is a measure of its capacity to elongate or stretch and is an indication of the ability of the material to flow and thereby mend a rupture in the surface of the material. A briquette of the asphalt is pulled apart at a uniform rate, and the elongation, measured in centimeters, that occurs before rupture takes place is called the ductility. The test is usually conducted at 77°F., and the briquette is pulled apart at a uniform rate of 5 cm. per minute. *Penetration* tests are made with a penetrometer which allows a needle or cone to penetrate the material without mechanical friction and is arranged to read the depth of the penetration in hundredths of a centimeter. A standard needle is used for asphalt materials[1] (D5-25), and the common test conditions are temperature, 77°F. (25°C.); time, 5 sec.; and load, 100 g. Other test conditions are

Deg. F.	Load, g.	Sec.
32	200	60
115	50	5

For greases and petrolatum[1] (D217-38T) the needle is replaced with a standard cone. The procedure is the same as for asphalt materials except that the temperatures of 32 and 115°F. are seldom used.

Road oils are examined for their asphalt content; Furol viscosity at 122 or 210°F.; and solubility in carbon disulfide,[5] carbon tetrachloride[1] (D165-27), and petroleum ether.[5] The asphalt content (D243-36) is determined by an evaporation test. A 100-g. sample of the oil is heated at 480 to 500°F. until the residue has a penetration of 100 at 77°F. This test sometimes ruins the ductility of the asphalt, and hence the value of the test is being questioned.

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[5] Methods of Sampling and Testing Highway Materials, *U.S. Dept. Agr. Bull.* 1216, 1928.

Gum in Gasoline.—The determination of gum in gasoline has been a troublesome test. The copper dish method of determining gum has been replaced by a method[1] (D381-36) that utilizes a measured and heated stream of air to assist in the vaporization. This test indicates the amount of gum at the time of test and the amount of deposition that may take place in service if the gasoline is used immediately. In addition, a test for *gum stability*[1] (D525-39T) which involves heating the gasoline at 211.5°F. in a bomb at a pressure of 125 lb. per square inch for 10 min. and then at 100 lb. per square inch, all in an atmosphere of oxygen, is useful in estimating the amount of gum that will be formed during storage. In this test the gum stability is indicated by the rate at which the pressure decreases or the rate at which oxygen is consumed. These tests are a great improvement, but it can still be said that a gasoline that has a low copper dish gum content is a thoroughly safe gasoline.

Procedures for Other Common Tests[1]

1. Burning quality of kerosene oils (D187-39).
2. Burning quality of long-time burning-oils (D219-36).
3. Carbon residue (Conradson carbon) of lubricating oils (D189-39), and Ramsbottom method (D524-39T).
4. Distillation of tars or pitches (D20-27T).
5. Doctor test.
6. Emulsion, steam of lubricating oils (D157-36).
7. Flash-point of volatile flammable liquids (D56-36), tag tester.
8. Float test for bituminous materials (D139-27).
9. Gum stability of gasoline (D525-39T).
10. Loss on heating asphalt or oil (D6-39T).
11. Melting-point of paraffin wax (D87-27).
12. Melting-point of petrolatum (D127-30).
13. Neutralization number (D188-27T).
14. Vapor pressure of natural gasoline, Reid (D323-39T).
15. Water and sediment by centrifuge (D96-35).
16. Precipitation number of lubricating oils (D91-35).
17. Saponification number (D94-39T).
18. Tetraethyl lead in gasoline (D526-39T).

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CHAPTER VI

DESIGN DATA AND THE LABORATORY

From the discussion in the previous chapter it is apparent that routine tests are not always suitable as a basis for engineering calculations. In this chapter a general scheme of obtaining engineering design data is presented. In general, only the methods that are of broad applicability will be discussed. Some requirements of engineering analysis methods follow:

1. The results must represent yields and properties that can be duplicated in a modern, properly operated commercial equipment.
2. The method must be such that it can be reproduced easily and quickly.
3. The cost must not be excessive.
4. The equipment should produce fractions or products that are large enough for the determination of gravity, viscosity, flash-point, etc.
5. The data should be general in nature, if that is possible, so that many possible combinations of yields can be computed from a single analysis.

The true-boiling-point method of analysis meets most of these requirements, but the Hempel distillation and other less elaborate distillations do not. Even a replica plant fails to meet the requirements of cost and of general usefulness. Obviously, the laboratory evaluation methods presented here and in Chap. VII are of little significance unless governed by the specifications of products as outlined in Chap. IX.

Replica Plants.—A direct means of estimating the yields and properties of desirable products is by the construction and operation of a laboratory-size apparatus that is a replica in all essential details of the proposed commercial installation. Excellent results can be obtained from a carefully built replica plant; but the plant is expensive, and its operation demands more time than is usually available. Occasionally a complete study of the operating conditions of a process is desired, and in such an instance the replica plant is obviously useful. It must be designed so that it actually duplicates plant results, or its usefulness is lost. Compared with the cost of commercial operation, the operation of a replica plant is not expensive and the results obtained from one carefully operated are probably more accurate than those obtained in most commercial operating tests. However, the operation of a replica plant is even more difficult than commercial operation, and carelessness may result in misleading data.

Universal Design Data.—In the operation of the replica plant only one set of yields, properties, and conditions can be obtained during a single "run," or test, and hence several runs must be made to obtain a complete set of results. For this reason many designers have adopted a more fundamental type of analysis which provides a more complete set of yields and properties. A discussion of the obtainment of this type of data is the purpose of this chapter. The extensive usefulness of this type of data, both in design and in operation, will be more apparent in Chap. VII. The methods outlined in this chapter provide a means of obtaining comprehensive design data, but they do not provide complete operating data. The replica plant is perhaps the best method of obtaining operating data from laboratory tests. The A.S.T.M. has adopted only one evaluation specification (D285-36), *i.e.*, distillation of crude petroleum for naphtha content.

A complete analysis, for design and operating purposes, should at least consist of the following data:

1. A distillation curve obtained by carefully fractionating the oil sample. This type of curve will be referred to as a *true-boiling-point curve*. The curve is obtained in a batch distillation in which each fraction or compound is carefully fractionated before it is allowed to leave the equipment.
2. A distillation curve obtained under equilibrium vaporization conditions. The vapor is not separated from the liquid until the desired equilibrium temperature is attained. This curve will be referred to as the *flash-vaporization curve*.
3. Mid per cent property curves which show the properties of the small amount of material that distills at any percentage. Common mid per cent curves are
   - *a*. Gravity mid per cent—specific gravity of fraction, versus mid per cent of fraction.
   - *b*. Viscosity mid per cent—viscosity at 100 or 210°F. of fraction, versus mid per cent of fraction.

   These curves are called mid per cent curves because the property is plotted at the mid percentage of the fraction that it represents. This type of curve is sometimes referred to as a "stream" curve, *e.g.*, specific gravity (stream).

4. Cumulative property curves which show the average properties of the entire material distilling to a given percentage or, more often, the average property of the residue at any percentage distilled. Common yield curves are
   - *a.* Viscosity yield—viscosity of residue versus per cent of residue.
   - *b.* Penetration yield—penetration of residue versus per cent of residue.
   - *c.* Flash-point yield—flash-point of residue versus per cent of residue.
   - *d.* End-point yield—end-point of gasoline versus per cent of gasoline.

The True-boiling-point Curve.—A true-boiling-point[1] curve is obtained by separating the liquid into nearly pure hydrocarbons[2] by distillation and fractionation and plotting the temperature of the vapor against the percentage. In order to obtain a thorough separation of hydrocarbons, an elaborate fractionating column is necessary. The best known of these types of columns are the Peters' true-boiling-point apparatus[1] for gasoline and heavier oils and the Podbielniak fractional-distillation apparatus[3] for heavy oils, gasoline, and natural gas. Many other equipments, which will accomplish practically the same results, are used by various refiners,[4] but they have not received names because they are not generally used. Several true-boiling-point curves are plotted in Fig. 8.

True-boiling-point Apparatus.—An apparatus of the Peters type is shown in Fig. 9. The fractionating column differs from most laboratory columns because it is completely insulated from the surroundings. The outer jacket *A*, through which heated air flows, is kept at substantially the same temperature as the temperature of the vapor within the column, so that no heat passes into or out of the fractionating column. The column is then said to operate under adiabatic conditions. Inasmuch as no heat is lost or gained by the column, the amount of reflux or cooling material that is introduced into the top of the column by the reflux air-jacket C is dependent only upon the composition of the vapor from the flask and the degree of separation desired. If the fractionating column is insulated with only an insulating material, the distillation and the amount of reflux required are directly subject to fluctuations in the condition of the environ-

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[1] PETERS and BAKER, *Ind. Eng. Chem.*, **18**, 69 (1926). The term true-boiling-point was first introduced by Peters in connection with the chemical distillation industries.

[2] The continuous character of the true-boiling-point curve for complex oils indicates that pure compounds are not produced. If pure compounds were produced, the curve would be made up of a series of steps, each flat step representing the boiling-point of a compound. Distillation curves of natural gas, natural gasoline, etc., by the Podbielniak fractional-distillation equipment do show these steps. However, crude oils are exceedingly complex materials, and the quantity of any compound is so small that the flat step for each one of them is not evident.

[3] Apparatus and Methods for Precise Fractional Distillation Analysis, *Ind. Eng. Chem., Anal. Ed.*, **3**, 177 (1931); Apparatus for Precise High-temperature Fractionation of Complex Liquid Mixtures, *Ind. Eng. Chem., Anal. Ed.*, **5**, 119, 135 (1933).

[4] BEISWENGER and CHILD, True Boiling Crude Analysis, Petroleum Division, Am. Chem. Soc., Atlanta Meeting.

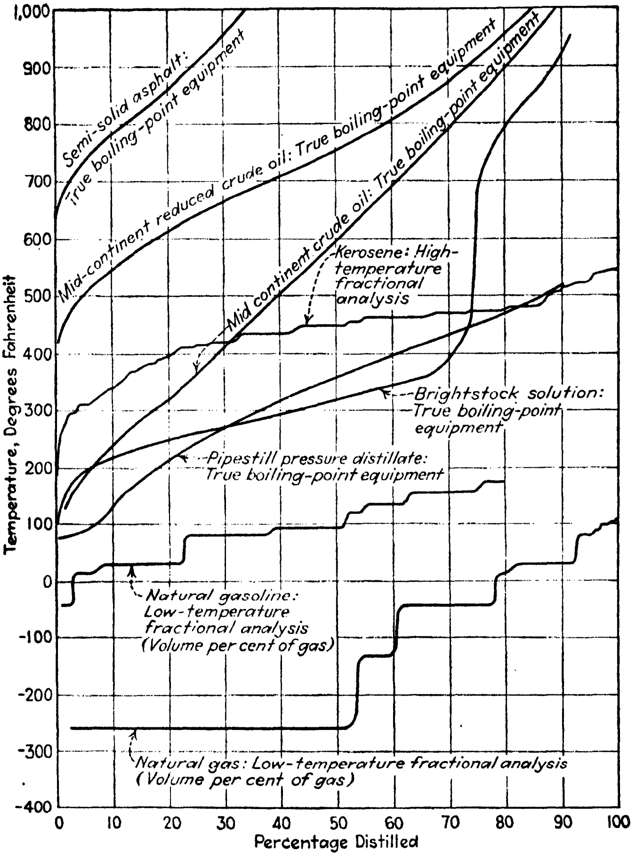

FIG. 8.—True-boiling-point distillation curves.

ment, such as the room temperature and draughts of air, and to fluctuations in the rate at which heat is supplied to the flask or still. With the adiabatic jacket these fluctuations can be brought within control. The disturbing influence of changing room conditions is particularly important in the operation of laboratory equipment, because the heat losses, even though the equipment has been carefully insulated, are often larger than the useful heat input.

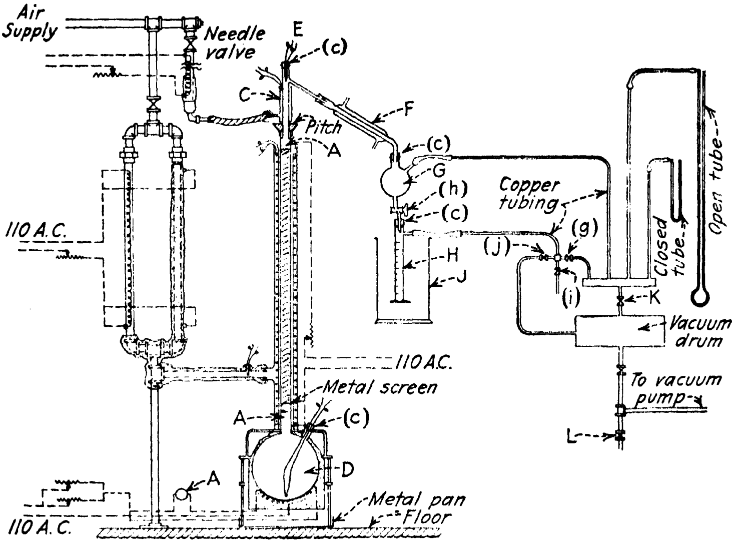

FIG. 9.—Diagram of a true-boiling-point apparatus.

The true-boiling-point still consists of a flask *D* (Figs. 9, 10) ranging in capacity from 1,000 to 5,000 cc. The larger still is advisable for the evaluation of heavy stocks, because fractions of 100 cc. are required for the determination of gravity, viscosity, flash-point, etc. However, the obtainment of very low pressures is difficult in the larger still unless a large vacuum pump is available. A vacuum pump having a displacement of 2 to 3 cu. ft. of air per minute is large enough for the 1,000-cc. still, but the larger still requires a pump having a displacement of at least cu. ft. per minute. Heat is supplied throughout the entire apparatus by electrical resistance coils. The mixture of vapor that is generated in the flask ascends the adiabatic column *A* and is fractionated into pure compounds by the principles outlined in Chap. XV. At the top of the column the vapor is cooled by the reflux air-jacket *C* so that most of it condenses and is returned to the column as reflux. The purified vapor passes the thermocouple *E* in the column head and is condensed in the water- or air-cooled condenser *F*. Near the end of the distillation the condensate may contain wax, and no cooling water is required for the condenser.

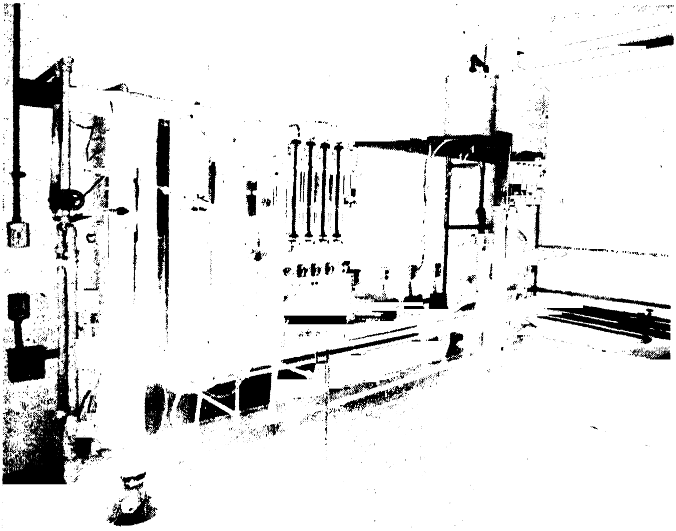

FIG. 10.—True-boiling-point vacuum still for charging 3,000 cc. The small still in the corner is a true-boiling-point still for distilling gasoline at atmospheric pressure. (*A. J. Smith Engineering Company.*)

The temporary receiver *G* is for operation at reduced pressure. During vacuum distillation the product normally drips through the receiver *G* into the graduate *H*. When the graduate is full, the stopcock *h* and the cock *g* are closed, and the graduate is removed by venting to the atmosphere through cock *i*. After an empty graduate is in position, the cock *j* is slowly opened so that the vacuum on the main system is not violently disturbed. An auxiliary vacuum pump may also be used to evacuate the graduate. After the graduate has been evacuated, cock *j* is closed and the cocks *g* and *h* may be opened again. Throughout the entire operation of changing the graduate, the pressure-regulation valve *K* need not be touched. Fine regulation of the pressure is obtained by means of the valve *K*, but for large adjustments of the pressure; *i.e.*, at pressures above 50 mm., the valve *L* located near the pump may be used. A small amount of noncondensable vapor is always present during distillation, and this vapor passes through valve *K* causing the throttling action that is necessary for regulation of the pressure. Manometers are used to measure the pressure in the equipment and in the graduate while it is being evacuated. When the equipment is operated at atmospheric pressure, the first product may be volatile, and, if so, the graduate should be immersed in the removable ice-bath *J*. Many materials have been used for sealing the corks *c*, etc., but LePage's glue, although it must be frequently applied, appears to be most satisfactory.

The distillation may be conducted in two ways, *viz.*, at a constant or at a variable rate of distillation. The more common method of operation is to collect the distillate at a constant rate. The curve obtained by this manner of operation is smooth, with the exception of slight irregularities, and is more convenient for design purposes than one that shows flat steps for each component. The method does not accomplish such good fractionation as the second method of operation in which the rate of distillation is governed by the amount of material that boils at each temperature. If the amount of material that boils at a given temperature is great, the rate should be fast; but if little material boils at the temperature, the rate should be slow, so that a higher reflux ratio is maintained.

The curves in Fig. 8 by the Podbielniak equipment were obtained by the second method of operation. At present, our knowledge of the theoretical behavior of complex mixtures and of the individual components that constitute complex oils is so meager that the more exact curve, obtained by the variable rate of distillation, is almost useless. When our knowledge is extended, and this is rapidly taking place, the more exact curve showing the percentage of each hydrocarbon will be of great value. The variable rate of distillation is useful in the preparation of pure compounds.

When the column is operated by the constant-rate method, the rate of heating should be such that distillate is collected at the rate of 1 per cent in 2 min. for atmospheric distillations and 1 per cent in 3 to 5 min. for vacuum distillations. The temperature of the air that enters the bottom of the column jacket should be about 5° below the flask temperature, and the temperature of the air leaving the jacket should be about 5° higher than the vapor-temperature in the column head. If the air loses heat too rapidly in the jacket, more air may be used; and if this fails to sustain the temperature, the resistance wires, strung within the jacket, may be heated. The quantity of cooling material or reflux that is used should always be the maximum amount that the capacity of the column will permit. At all times the packing of Lessing rings in the column should be wet with liquid. However, if too much reflux is used, the column will "flood" or "prime," and reflux will accumulate in it to such an extent that vapor cannot pass up it without carrying the liquid with it. Finally, if flooding persists, the column fails to function as a fractionating device, and the reflux liquid is carried into the condenser.

High-boiling Materials.—Even though a pressure of 0.5 mm. of mercury may be maintained in the true-boiling-point column, the highest boiling oils, such as brightstock and tar, cannot be completely vaporized. The highest vapor-temperature that can be obtained in the true-boiling-point apparatus is approximately 1000°F. when corrected to atmospheric pressure (Fig. 52, page 131). However, when very short-boiling-range products (approximately 300°F.) are being distilled, a temperature of 1060 or even 1100°F. may be attained without decomposition. In evaluating heavy lubricating-oil stocks, a narrow-boiling-range sample must be prepared, because a vapor-temperature of at least 1040°F. is necessary in order to evaluate heavy lubricating oils. To produce such a charge-stock, the volatile low-boiling and the tarry high-boiling portions of the lubricating-oil sample must be removed. The light portions of the sample may be removed by a steam-atmospheric fractionating distillation in a laboratory shell-still. The residue from this "topping" operation may be separated into a narrow-boiling-range lubricating oil stock and a residual tar or "bottoms" product by a continuous vacuum-flash distillation. The "heart-cut" lubricating stock may be readily evaluated for lubricating oils by a true-boiling-point analysis. This heart-cut lubricating stock is particularly suitable for analysis because it contains no tarry material, and therefore the bottoms from the subsequent true-boiling-point analysis is a clean, heavy-cylinder stock.

As an example, we may wish to evaluate the lubricants in a Mid-Continent reduced or topped crude oil of 26 A.P.I. gravity. By a steam-atmospheric distillation in a small shellstill a 23 A.P.I. reduced crude-oil and a 32 A.P.I. gas-oil distillate may be produced. The 23 A.P.I. reduced crude oil is then distilled in the vacumm-flash vaporizer (Figs. 11, 12), leaving as a residue a 9 A.P.I. tar and obtaining as a distillate a 25 A.P.I. heart-cut lubricating-oil stock which is suitable for evaluation in the true-boiling-point column. The percentage "break-up" would be approximately as follows:

Material	Per cent	A.P.I.
Gas oil	20	32
Lube stock (heart-cut)	73	25
Tar	7	9
Reduced crude (charge-stock)	100	26

Continuous Vacuum-flash Vaporizer.—The flash vaporizer must be large, because small vaporizers cannot be easily controlled. However, a small one similar in principle to the equilibrium vaporizer shown in Fig. 13 might perform properly. A satisfactory flash vaporizer is shown in Figs. 11 and 12. In Fig. 12 it is situated to the right, and the control desk and panel are in the center.

The purpose of the flash vaporizer is to prepare a lubricating stock for evaluation purposes, and hence the residue of tar should be as small as possible and should contain no lubricants that can be removed from the tar in a commercial vacuum plant. For this reason the apparatus is always operated at the maximum allowable temperature of about 700°F.[5] and at as low a pressure as possible. With an almost leak-free apparatus and with a vacuum pump having a capacity of approximately 9 cu. ft. per minute the apparatus can be operated at a pressure of 7 mm. The capacity of the equipment ranges between 1 and 4 gal. per

[5] Decomposition or cracking starts at 680°F.

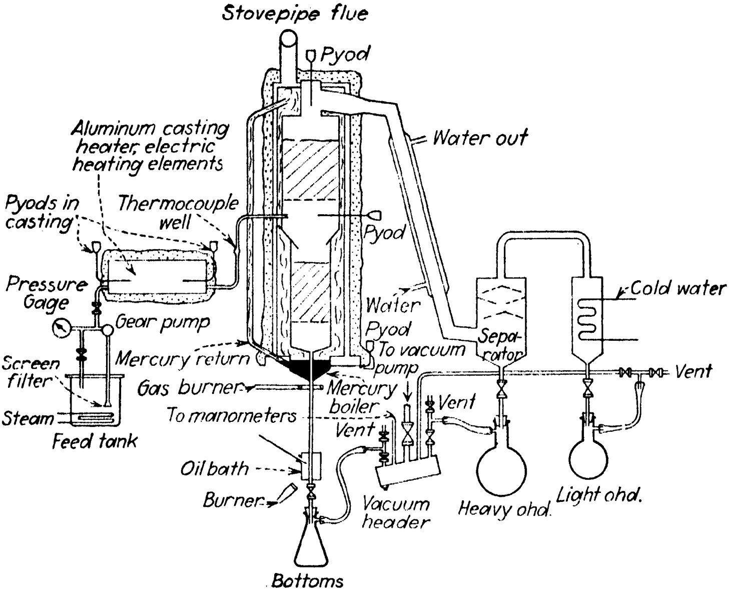

Fig. 11.—Diagram of continuous vacuum-flash equipment.

Fig. 12.—Continuous-flash vaporizer. (Two small shellstills are shown at the left.) (*A. J. Smith Engineering Company.*)

hour depending upon the character of the charging-stock. The aim is to vaporize as large a percentage of oil as possible, even though the fractionation is imperfect, and hence no more reflux is used[6] than the small amount that is required to prevent entrainment of tar into the distillate.

The continuous vacuum-flash vaporizer is essentially a replica of a modern vacuum distillation plant, but its usefulness is not limited to such operations. The pipestill of the commercial unit is replaced by a coiled-steel heating tube cast in aluminum. Insulated resistance heaters are also embedded in the casting, and they are connected to an automatic temperature controller. The use of a casting as a heating agent has several advantages. It serves as an excellent reservoir for heat so that large fluctuations in temperature are impossible; it facilitates the transfer of heat from the resistance heaters to the oil; and its temperature can be easily controlled by an automatic controller acting upon one of the resistance heaters. Heat losses are abnormally high in small equipment, and hence the vacuum-tower is jacketed with mercury vapor and with flue gas. The temperature of the mercury jacket can be automatically controlled by regulating the pressure at which the mercury boils.

Equilibrium-flash Vaporizer.—If a liquid mixture is heated without allowing the vapor to separate from the unvaporized liquid until the final desired temperature is reached and if the two phases, liquid and vapor, are kept in intimate contact, the vaporization occurs by an equilibrium flash. By this method the temperature required to vaporize a given percentage is much lower than that required in vaporizing the same amount by a true-boiling-point or A.S.T.M. distillation. This difference may be explained by considering that the vapor acts as an inert gas and tends to vaporize the remaining liquid as does steam in a steam distillation.

Inasmuch as the continuous-flash process of vaporizing is used in almost all modern distillation plants, equilibrium-flash data are vitally important. Furthermore, as outlined in Chaps. XIV and XXIII, such data are important in other phases of design work.

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[6] Operation with very little or no reflux at the vaporizer section of a tower is common commercial practice in the operation of atmospheric as well as vacuum plants. Usually very little reflux finds its way into the vaporizer section. However, a little fractionation does occur in the plates between the vaporizer and the first side-draw plate because of heat losses. This reflux is probably little more than that required to stop entrainment and to keep the plates sealed with liquid.

If the oil is "flashed" at one temperature, a certain percentage of it is vaporized; and by flashing at several temperatures a complete curve relating the flash temperature and the percentage vaporized may be obtained. Such a curve is called the flash-vaporization curve. Figure 13 is a sketch of a laboratory equipment for the determination of equilibrium-flash data. Successful flash-vaporization equipment must be capable of feeding a small amount of material at a constant rate and of heating it to a constant temperature. At the same time an equilibrium or intimate contact must be established between the liquid and the vapor at the flash temperature. The vaporizer A, packed with Lessing rings, is provided for establishing equilibrium. The rate of feed is regulated by the constant head device D and the orifice E. A constant rate depends upon a constant feed temperature, because the viscosity and the rate of flow through the orifice vary with temperature. Constancy of the flash temperature is maintained by the resistance coil that surrounds the heating tube and particularly by the glass heating tube in the vapor jacket. Should the temperature of the oil leaving the

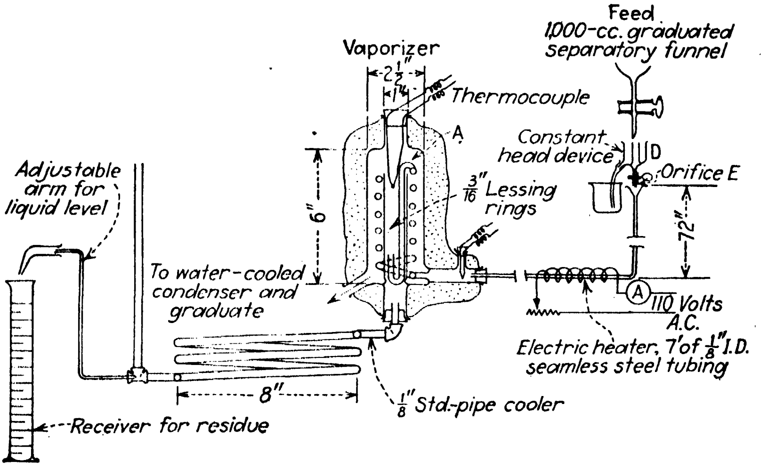
Feed
1,000-cc. graduated separatory funnel
Vaporizer
2 1/2"
1 1/4"
Thermocouple
A
Constant head device
D
Orifice E
6"
3/16" Lessing rings
72"
Adjustable arm for liquid level
To water-cooled condenser and graduate
A
110 Volts A.C.
Electric heater, 7' of 1/8" I.D. seamless steel tubing
8"
1/8" Std.-pipe cooler
Receiver for residue

FIG. 13.—Equilibrium-flash vaporizer.

steel heating tube be slightly high, the oil will be cooled in the glass coil by the vapors, and vice versa.

The apparatus described (page 62, Fig. 13) does not provide such exact results as do other types of equipment,[7,8] but the data are sufficiently accurate for most design work. The more exact equipments[7,8] consist of a large bath which keeps the heating coil and vaporizer at a constant temperature. The temperature of the bath can be controlled within ±0.5°F. The objection to such equipments for commercial work is the length of time required to make an analysis. The temperature of the bath changes very slowly, and a large sample of oil is required.

A series of orifices having holes ranging from ¼ to 2 mm. in diameter are necessary in order to handle the complete range of charging-stocks. The apparatus gives equilibrium conditions when operating at capacities of about 9 to 19 cc. per minute. A constant condition can be obtained in approximately 20 min. of operation, but at least 40 min. is required for the determination of a single point on the flash-vaporization curve. In processing light materials such as gasoline, the distillate receiver should be immersed in a brine bath or even a carbon dioxide snow-container to condense the volatile hydrocarbons. Modifications can be made for the determination of flash-vaporization data at reduced pressures.

Fractional Analysis.—The Podbielniak low- and high-temperature precision fractional-distillation equipments[3] can be used to obtain this type of analysis. The fractional analysis may be defined as one that states the percentage of each compound in the sample. For relatively simple mixtures, such as natural gas, natural gasoline, lacquer thinners, and short-boiling-range petroleum fractions, the fractional analysis is of great importance (Fig. 8).

Figures 14 and 15 indicate details of the Podbielniak equipments. They are both essentially true-boiling-point equipments, but the low-temperature apparatus is modified so that it can be operated at temperatures far below zero. In the true-boiling-point apparatus discussed on the previous pages the pressure is

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[7] LESLIE and GOOD, The Vaporization of Petroleum, *Ind. Eng. Chem.*, **19**, 453 (1927).

[8] PIROMOOV and BEISWENGER, Equilibrium Vaporization of Oils . . . , *A.P.I. Bull.* 10, No. 2, Sec. II, p. 52, 1929.

usually not changed during the distillation, but in the fractional-analysis equipments the pressure and temperature may be changed simultaneously. In the low-temperature equipment the sample may be cooled with liquid ethylene, ethane, air, nitrogen, carbon dioxide, etc. Gas samples of 2,000 cc. are advisable, although samples of only 100 cc. have been successfully analyzed by the use of a microfractionating tube. Liquid samples of 50 cc. are desirable. The high-temperature equipment[9] may be obtained with flasks having capacities from 250 to 2,000 cc.

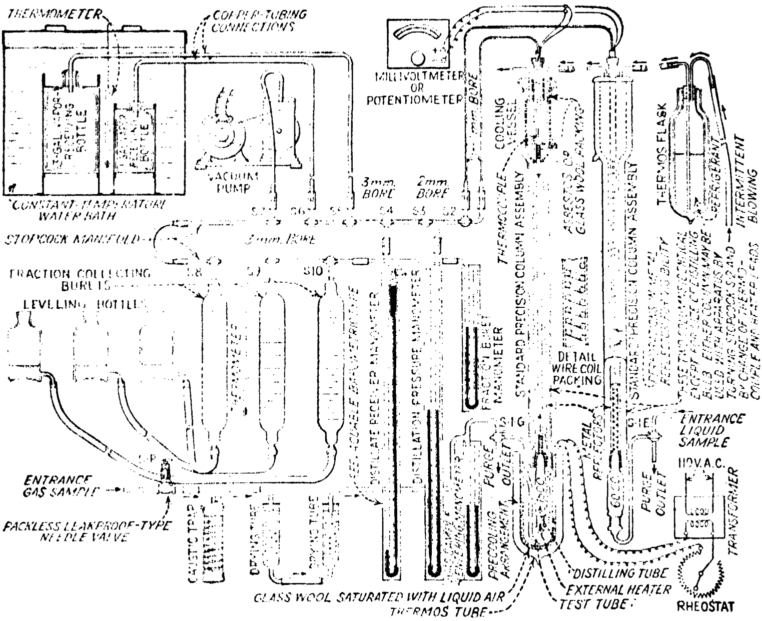

Fig. 14. Podbielniak low-temperature precision fractional-distillation apparatus. (*Walter J. Podbielniak.*)

In analyzing gases (Fig. 14) the sample is introduced into the chilled distilling bulb, and all gas except the air, hydrogen, and methane is condensed. These permanent gases are collected in an evacuated receiver, and the pressure in the receiver is recorded. The condensed hydrocarbons are then allowed to warm, and the components are fractioned and collected one by one in evacuated receivers. Heat may be required to vaporize the highest boiling part of the liquid. When a flat place occurs in the distillation curve or, in other words, material is collected at a constant

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[9] Podbielniak Industrial Research and Analytical Laboratories, Chicago.

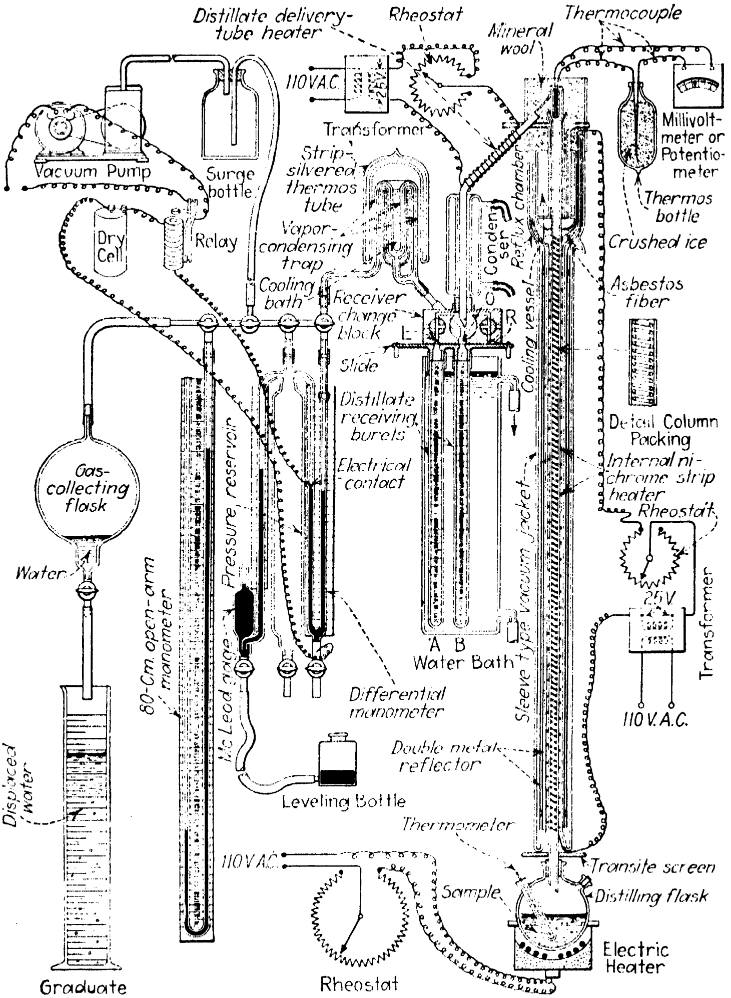

Fig. 15.—Podbielniak high-temperature precision fractional-distillation apparatus. (*Walter J. Podbielniak.*)

temperature, the reflux is decreased by allowing the component to escape from the column more rapidly. As the temperature tends to rise, the reflux is increased by using a slower rate of distillation until finally little or no more material collects. At the same time the pressure in the column tends to drop. This condition indicates that one component has been removed. The components may be collected in different receivers; but more often the gas is collected as a mixture, and the percentage of each component is determined by examining the distillation curve.

The volume of each component can be measured in mol or volume percentage by merely noting the change in pressure in the gas receiver, because the temperature and the volume of the receiver remain constant during the test.

Auxiliary Equipment.—In completing an evaluation of an oil stock, the fractions obtained in a true-boiling equipment are examined to determine their properties such as the gravity, viscosity, flash-point, and penetration (Chap. VII). The largest practical size of fraction is about 100 cc., and hence special microanalysis equipments are sometimes useful. The gravity may be obtained with 4-in. hydrometers and more accurately with a chainomatic specific-gravity balance. By careful management the standard viscosity equipment may be used, but viscosity pipettes[10] similar to the Ostwald pipette are useful.

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[10] A.S.T.M. Petroleum Products and Lubricants, D445-39T, 260 South Broad Street, Philadelphia, Pa.

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CHAPTER VII

THE EVALUATION OF OIL STOCKS

There are three general classes of crude oils: paraffin base, mixed base, and asphalt base. In addition, Lane and Garton[1] suggest other modifications, *e.g.*,

A. Paraffin base.
B. Paraffin-intermediate base.
C. Intermediate-paraffin base.
D. Intermediate (mixed) base.
E. Intermediate-naphthene base.
F. Naphthene-intermediate base.
G. Naphthene (asphalt) base.

Thus, paraffin-intermediate-base (B) oil contains paraffin-base gasoline and intermediate-base lubricants—and base E oil contains intermediate-gasoline and naphthene lubricants. Crude oils of bases A and C are most typically paraffin base, and oils of bases E and G are typically naphthene base. An oil that contains wax is designated as "wax bearing."

Although the base of an oil indicates some of the general properties of the oil, no classification of crude oils can be entirely satisfactory. This is because few oils belong distinctly to any one group, and some oils have such intermediate properties that they are misfits in any group. Nevertheless, to experienced men, the base of an oil connotes certain distinctive properties. These are indicated in the following discussion.

The Base of a Crude Oil.—There are several common methods of judging the base of an oil. These tests or inspections should be used collectively because an oil may be of one base by one test and belong to another base by other tests. In other words, an oil may be on the border line between two bases, and the classification of it should depend somewhat upon the particular properties that are of greatest interest.

1. The Bureau of Mines "Key Fraction No. 1"[2] is the portion of a crude oil that boils between 482 and 527°F. If the gravity

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[1] "Base" of a Crude Oil, *U.S. Bur. Mines, Repts. Investigations* 3279, 1935.

[2] SMITH, N. A. C., The Interpretation of Crude Oil Analyses, *U.S. Bur. Mines, Repts. Investigations Serial* 2806, 1927.

of this fraction is above 40 A.P.I., the oil is paraffin base; and if its gravity is below 33 A.P.I., the oil is naphthene base. In general this checks with the correlation of crude oils by gravity, as presented in Fig. 20.

2. The Bureau of Mines "Key Fraction No. 2"[2] is that portion of a crude oil which boils between 527 and 572°F. at 40 mm. pressure. By the correction chart (Fig. 52, page 131) the boiling-range at 760 mm. is 733 to 779°F. If the cloud-point of this fraction is below 5°F., the crude oil contains substantially no wax and is distinctly naphthene or intermediate-naphthene base. However, if the cloud-point is above 5°F., the oil is designated as wax bearing.

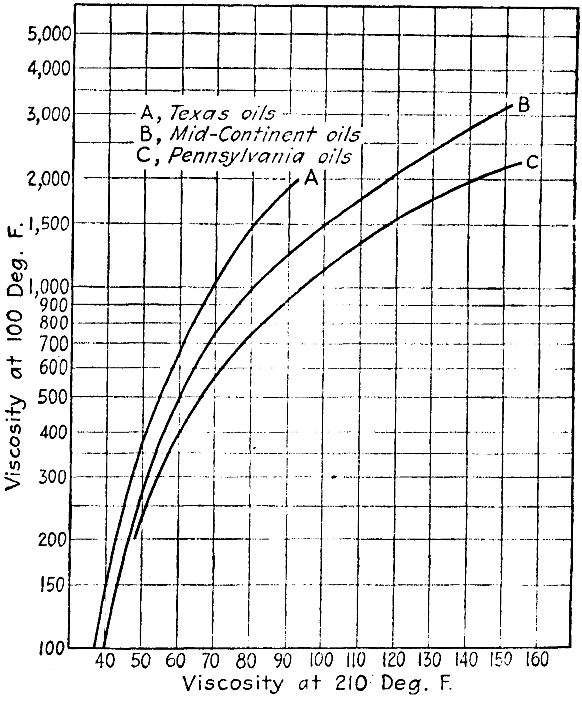

FIG. 16.—Relation of viscosity at 100°F. to viscosity at 210°F.

3. The viscosity-temperature-relation of an oil is perhaps the most important property in the valuation of oil stocks. At high temperatures the viscosity of an oil and its ability to lubricate surfaces become less. Those oils whose viscosity decreases

rapidly with temperature are not so desirable as oils that retain their viscosity. According to Fig. 16 the paraffin-base oils lose less viscosity with an increase in temperature than do other types of oil. The viscosity-temperature-relation is an important property; and inasmuch as the market price is largely determined by this property, it may eventually become of even more importance than the base of an oil. Recently, lubricating oils have been produced by the polymerization[3] of unsaturated light oils, by hydrogenation, and by solvent treating. Some of the oils by these methods exhibit viscosity-temperature-relations that are superior to those of paraffin-base oils.

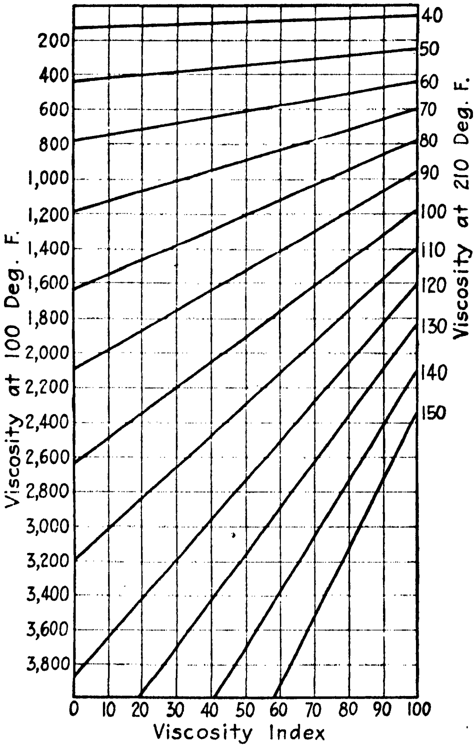

FIG. 17.—Viscosity index. (*Dean and Davis, Chem. Met. Eng.*)

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[3] SULLIVAN *et al.*, Lubricants from Cracked Distillates, *Oil Gas. J.*, June 4, 1931.

Dean and Davis[4] have suggested a useful constant, the *Viscosity Index,* for comparing the viscosity-temperature-relation of oils. A Pennsylvania or paraffin-base oil, with an arbitrary index of 100, was adopted as the standard high-index oil. At the other extreme is a naphthene-base oil with an index of 0. Figure 17 is a chart by which the Viscosity Index may be computed. As an example, the Viscosity Index of an oil having a viscosity of 90 at 210°F. and 1,200 at 100°F. is 79. The index was determined by following the oblique line marked 90 to the horizontal line marked 1,200. These lines intersect at the vertical line of 79 index.

The *viscosity-gravity constant*[5] is closely related to the Viscosity Index. The constant can be obtained from the gravity at 60°F. and the viscosity at 100°F., and in turn the Viscosity Index can be obtained from the viscosity-gravity constant. Thus the Viscosity Index for light lubricating oils and distillates can be obtained without determining the viscosity at 210°F. The viscosity at 210°F. of such oils cannot be accurately determined.

The well-fractionated narrow-boiling-range fractions obtained in a true-boiling-point distillation seem to have slightly higher Viscosity Indexes than regular blended oils. Figure 21 indicates higher indexes than those shown in Fig. 16.

4. The gravity versus gasoline content of a crude oil is a further indication of the base of the oil. More than 130 crude-oil analyses were used in plotting Fig. 18. The percentage of 410 to 425°F. end-point gasoline was plotted against the A.P.I. of the crude oil. The comparison indicates three well-defined zones for the different bases of oils. For example, a 36 A.P.I. crude oil containing 30 per cent 415°F. gasoline would be classed as a mixed-base oil.

5. A comparison of the properties of an unknown oil with those of known oils is a common method of studying an oil. A comparison of only two or three oils is not satisfactory and may lead to erroneous conclusions. Hence the following comparison of more than 82 true-boiling-point analyses of crude oils is presented. In all cases the properties are those of raw products just

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[4] Viscosity Variations of Oils with Temperature, *Chem. Met. Eng.*, **36,** 618 (1929); Applying Viscosity Index to the Solution of Lubricating Oil Problems, *Oil Gas J.*, Mar. 31, 1932, p. 92.

[5] McCluer and Fenske, *Ind. Eng. Chem.*, **24,** 1371 (1932).

as they were obtained from the true-boiling-point distillation equipment. A comparison of the properties of raw-oil samples is to be preferred to a comparison of finished-oil properties

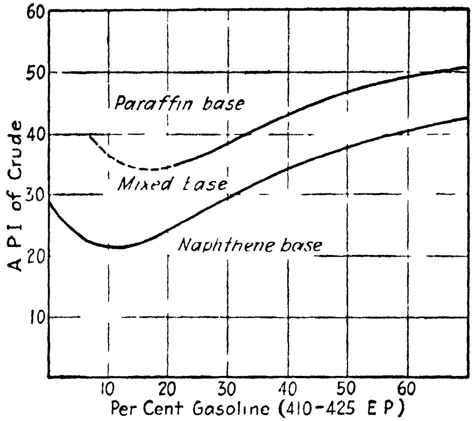

Fig. 18.—Base of a crude oil.

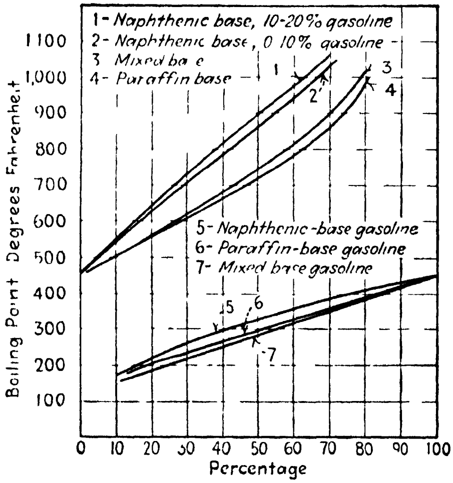

Fig. 19.—Correlation of the boiling points of crude oils.

because of the uncertainty introduced by laboratory treating and finishing operations.

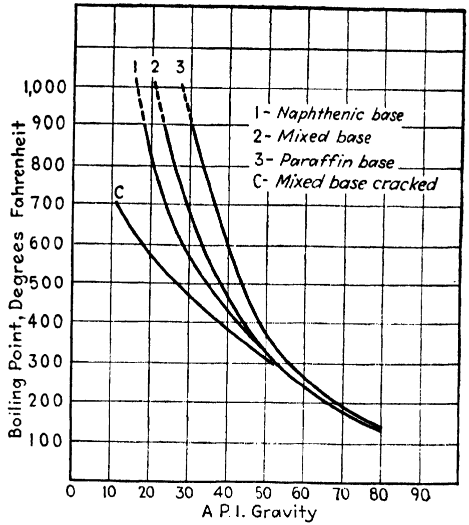

FIG. 20.—Correlation of A.P.I. gravity of crude oils.

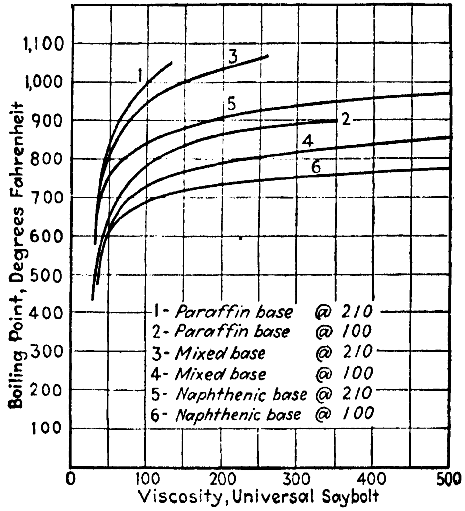

FIG. 21.—Correlation of viscosity of crude oils.

Figures 19, 20, and 21 are comparisons of the true-boiling-point distillation curves, the A.P.I. mid per cent gravity (see page 73), and the mid per cent viscosity (see page 73) of the various bases of crude oil. Figure 19 was obtained by plotting the boiling-range of the material boiling up to 450°F. as 100 per cent and the boiling-range of the remaining material, or base of the oil, as 100 per cent. By a reverse operation, an approximate true-boiling-point distillation curve can be computed if the percentage of 450°F. (about 428°F. A.S.T.M. end-point) material and the base of the oil are known. Figure 20 was obtained by plotting the A.P.I. gravity of the fractions of crude oil at their mid or 50 per cent boiling-points. A large change in the boiling-point of the higher boiling oils causes only a small change in the gravity, and hence the upper parts of the curves are not entirely dependable. Figure 21 was plotted similarly to Fig. 20, *i.e.*, by plotting the viscosities at 100 (and 210)°F. of the fractions at their mid boiling-points.

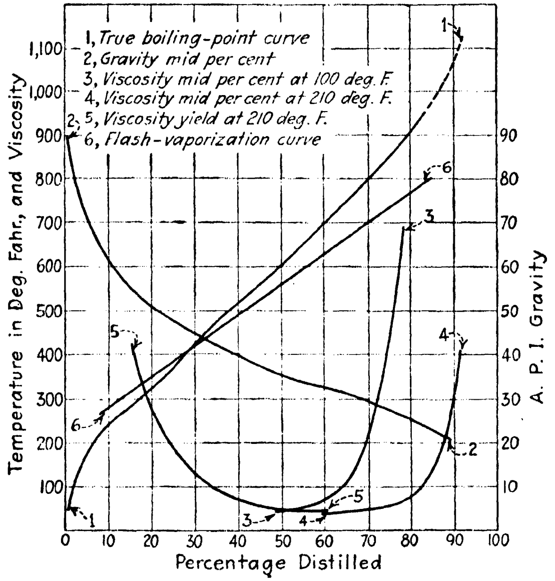

FIG. 22.—True-boiling-point evaluation curves for a 37.3 A.P.I. mixed-base crude oil.

These curves are merely averages of many crude oils, and perhaps no single crude oil will fall exactly on the average lines.

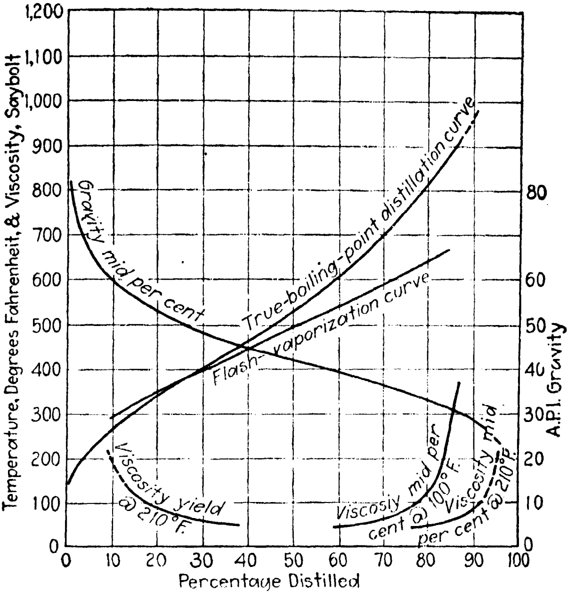

FIG. 23.—True-boiling-point evaluation curves for a 42.2 A.P.I. paraffin-base crude oil.

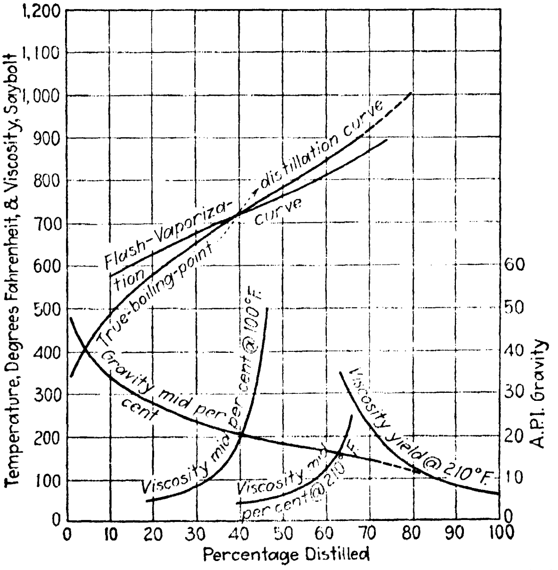

FIG. 24.—True-boiling-point evaluation curves for a 20.2 A.P.I. naphthene-base oil.

As mentioned before, crude oils are seldom found that are typically paraffin, mixed, or naphthene base. Figures 22, 23, and 24 are analyses of typical crude oils.

Example 3. Construction of Average Crude-oil Curves without Analysis. A crude oil contains 40 per cent gasoline and has a gravity of 38 A.P.I. According to Fig. 18 the oil is a typical mixed-base oil.

Computed data for true-boiling-point distillation curve (see curves 7 and 3, Fig. 19):

Per cent	Per cent of crude	Temperature, deg. F.
Gasoline:		
25	10	205
50	20	291
75	30	368
100	40	450
Base:		
20 $40 + 60 \div 5 =$	52	554
40	64	681
60	76	815
80	88	1020
100	100	

The gravity and viscosity data can be obtained from Figs. 20 and 21: The data for the mid per cent curves are as follows:

Temperature, deg. F.	Gravity, A.P.I.	Viscosity	
		At 100°F.	At 210°F.
150	75		
200	66		
300	52.2		
400	43.5		
500	38.5		
600	33.0	45	
700	29.3	76	
750	....	125	
800	26.0	233	48
850	....	490	63
900	22.7	...	76
950	....	...	105
1000	20.5	...	151
1050	...	...	238

6. The most useful method of cataloguing the base or paraffinicity of crude oil or any stock derived from it is the characterization factor.[6,7] This factor may be defined as the specific gravity (at 60°F.) divided into the cube root of the temperature (degrees Fahrenheit absolute). Typical factors for various stocks are

Paraffin hydrocarbons	12.7
Pennsylvania stocks	12.2–12.5
Mid-Continent stocks	11.8–12.0
Gulf Coast stocks	11.0–11.5
Cracked gasolines	11.5–11.8
Cracking plant feeds (combined)	10.5–11.5
Recycle stocks	10.0–11.0
Cracked residuums	9.8–11.0
Benzene	9.8

The factor has been made useful by relating it[7] to many of the physical properties of petroleum stocks (see Chap. VIII).

7. Another indication of the base of an oil is the "cast" or "bloom" of the lubricating oil stocks. By transmitted light the color of oils varies from a light yellow to a deep red. By reflected light the oil may exhibit a blue- or yellow-green appearance at the surface, regardless of color. This appearance is due to fluorescence and is called the cast of the oil. It may be noted by looking at the oil at an angle rather than directly through the oil or, even better, by viewing the oil in thin layers on a black background. Properly refined paraffin-base oils and even some mixed-base oils have a yellow-green cast, but naphthene oils appear deep blue. The natural yellowish cast of paraffin-base or mixed-base oils may be spoiled by improper acid treatment.

Typical Crude Oils.—In addition to the properties of crude oils that are inferred or illustrated in the discussion of the bases of crude oils, some of the characteristics[8] of the crude oils produced

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[6] WATSON and NELSON, Improved Methods for Approximating Critical and Thermal Properties of Petroleum Fractions, *Ind. Eng. Chem.*, **25**, 880 (1933).

[7] WATSON, NELSON, and MURPHY, Characterization of Petroleum Fractions, *Ind. Eng. Chem.*, **27**, 1460 (1935).

[8] NELSON, W. L., Percentage of Naphthenic Base Crudes Produced Declining, *Oil Gas J.*, July 29, 1937, p. 91.

in the United States from 1927 to 1936 are shown in Figs. 25 and 26 and in the tabulation given on pages 79 and 80. These data

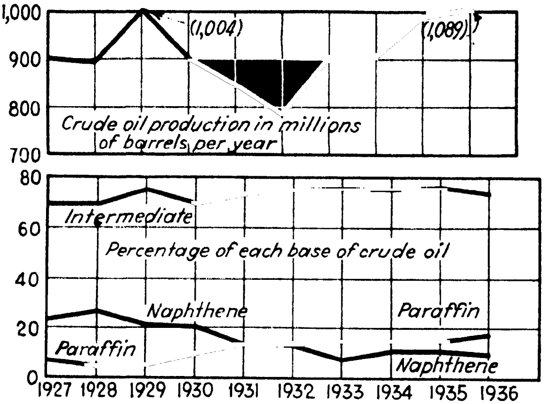

FIG. 25.—Yearly production and base of oil produced in the United States. (*Oil Gas J.*, July 29, 1937, p. 91.)

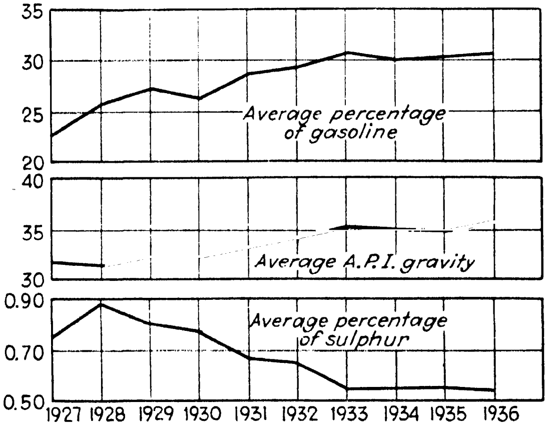

FIG. 26.—Average gravity, sulfur, and gasoline content of United States petroleums. (*Oil Gas J.*, July 29, 1937, p. 92.)

were compiled in a study of the 99 largest oil fields of the United States, and detailed statistics for each of the fields have also been published.[9]

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[9] NELSON, W. L., Six articles in *Oil Gas J.* (averaged by states) July 29, 1937, p. 91; (California) Aug. 5, 1937, p. 36; (Oklahoma) Aug. 19, 1937, p. 48; (Texas) Sept. 2, 1937, p. 50; (Kansas) Oct. 28, 1937, p. 48; (Louisiana and five other states) Nov. 4, 1937, p. 54.

PERCENTAGE OF EACH BASE OF OIL, BY STATES

	1927	1930	1932	1934	1936
California:					
Naphthene	40.3	26.8	25.6	29.0	26.6
Intermediate	59.6	73.2	74.4	71.0	73.4
Texas:					
Naphthene	21.8	29.6	10.2	5.9	6.6
Paraffin	20.1	7.2	10.5	7.0	8.1
Intermediate	58.1	63.2	79.3	87.1	85.3
Oklahoma:					
Paraffin	.....	24.0	32.8	48.6	49.8
Intermediate	100.0	76.0	67.2	51.4	50.2
Kansas:					
Intermediate	100.0	100.0	100.0	100.0	100.0
Louisiana:					
Naphthene	29.2	23.8	20.5	7.3	2.1
Paraffin	70.8	76.2	66.7	23.5	52.9
Intermediate	.....	.....	11.9	69.3	45.0
Miscellaneous:					
Naphthene	34.0	33.7	21.4	17.9	14.5
Paraffin	7.0	21.8	28.0	30.8	32.7
Intermediate	59.0	44.5	50.6	51.3	52.8
Total:					
Naphthene	23.8	20.4	12.8	10.4	9.7
Paraffin	7.1	9.9	12.5	14.3	16.7
Intermediate	69.1	69.7	74.7	75.3	73.6

PERCENTAGE OF GASOLINE AND NAPHTHA, BY STATES

	1927	1930	1932	1934	1936
California	17.5	24.4	26.7	25.3	26.4
Texas	23.8	22.6	30.0	32.4	31.8
Oklahoma	31.4	34.5	33.0	30.4	30.2
Kansas	32.4	32.0	33.5	36.0	39.3
Louisiana	16.2	18.1	18.7	22.8	25.8
Miscellaneous	16.7	22.5	25.8	26.5	27.6
Total	22.6	26.2	29.4	30.0	30.6

AVERAGE A.P.I. GRAVITY, BY STATES

	1927	1930	1932	1934	1936
California	24.6	28.2	29.5	28.8	29.3
Texas	32.6	31.3	35.7	37.1	35.8
Oklahoma	38.7	38.6	38.4	37.1	36.5
Kansas	37.8	37.6	38.1	38.9	39.6
Louisiana	30.9	31.6	32.2	35.5	41.6
Miscellaneous	27.4	31.3	33.7	34.2	35.0
Total	31.6	32.2	34.4	35.0	35.9

PERCENTAGE OF SULFUR, BY STATES

	1927	1930	1932	1934	1936
California	1.145	0.925	0.925	0.927	0.904
Texas	0.445	0.93	0.572	0.462	0.475
Oklahoma	0.328	0.334	0.292	0.266	0.258
Kansas	0.25	0.26	0.24	0.246	0.292
Louisiana	0.30	0.295	0.29	0.145	0.182
Miscellaneous	1.51	1.20	1.05	1.0	0.96
Total	0.75	0.771	0.645	0.545	0.546

The octane numbers of the gasolines from the several bases of crude oils are fairly well defined. From a limited number (41) of crude oils it appears that the octane numbers are somewhat as follows:

	Octane No. of 398 E.P. gasoline	
	Average	Range
Paraffin base	40.2	34–53
Paraffin-intermediate	45.3	41–50
Intermediate base	56.0	50–61
Naphthene and naphthene-intermediate	64.9	55–71

Fundamental Mathematics.—The physical properties of an oil are found to vary gradually throughout the range of compounds that constitute the oil. Distillation is a means of arranging these chemical compounds in the order of their boiling-points. The properties such as color, specific gravity, and viscosity are found to be different for each drop or fraction of the material distilled. The rate at which these properties change from drop to drop may be plotted as mid per cent curves (page 83) such as curves 2, 3, and 4 in Fig. 22.

The refinery engineer is most often interested in determining the property of a commercial fraction such as the gravity or viscosity. In reality, the gravity or viscosity of a fraction is an average of the properties of the many drops that constitute the fraction. If each drop is equally different from the last drop and from the succeeding one, then the drop that distills at exactly half of the fraction has the same property as the average of all of the drops. This would be the condition for a mid per cent curve that is a straight line. Mid per cent curves are never exactly straight lines (Fig. 27), but they are substantially straight through any short range of percentage. For a short range of percentage the average property is equal to the property at the mid-point of the fraction. Each short range of percentage may be considered as a material, and the arithmetical average of the properties of these materials is the property of the total fraction. The mechanism of using the foregoing principles can be best illustrated by an example:

Example 4. Use of Gravity Mid Per Cent Curve.—Compute the specific gravity of a 41.4 A.P.I. (0.8183 sp. gr.) mixed-base crude oil from the specific-gravity mid per cent curve. Figure 27 is the gravity mid per cent curve as determined in the laboratory.

Assume that the curve is broken up into 19 fractions as indicated in Fig. 27. The gravities of the 19 materials are indicated by the 19 short horizontal lines. The curve is substantially straight through fractions 5 to 18 inclusive, and the horizontal lines pass through the centers of these fractions. The horizontal lines (average gravities) for the other fractions (1 to 4 and 19) do not pass through the mid-point but are so arranged that the triangular areas above and below the curve are equal. The gravities of the 19 fractions are as follows:

Fraction No.	Range of percentage	Sp. gr.
1	0–5	0.6506
2	5–10	0.6936
3	10–15	0.7227
4	15–20	0.7420
5	20–25	0.7583
6	25–30	0.7720
7	30–35	0.7844
8	35–40	0.7958
9	40–45	0.8067
10	45–50	0.8170
11	50–55	0.8280
12	55–60	0.8388
13	60–65	0.8498
14	65–70	0.8602
15	70–75	0.8713
16	75–80	0.8827
17	80–85	0.8939
18	85–90	0.9065
19	90–100	0.9340

The gravity of the crude oil is equal to five times that of each of the fractions 1 to 18 inclusive plus ten times the gravity of fraction 19, all divided by 100. The computed gravity is 0.8171, and the actual gravity of the crude oil was 0.8183. This is a reasonable check and is sufficiently accurate for most engineering design work.

This crude oil contains 40 per cent gasoline, 15 per cent kerosene, 15 per cent gas oil, and 30 per cent reduced crude oil. The gravity of the gasoline equals five times the gravity of fractions 1 to 8 inclusive divided by 40 and numerically is 0.7399 (59.8 A.P.I.). In a similar manner the gravity of the kerosene is equal to five times the gravity of fractions 9, 10, and 11 divided by 15 and is 0.8172 (41.6 A.P.I.). Likewise the gravity of the gas oil and reduced crude oil are respectively 0.8496 (35 A.P.I.) and 0.9037 (25.1 A.P.I.).

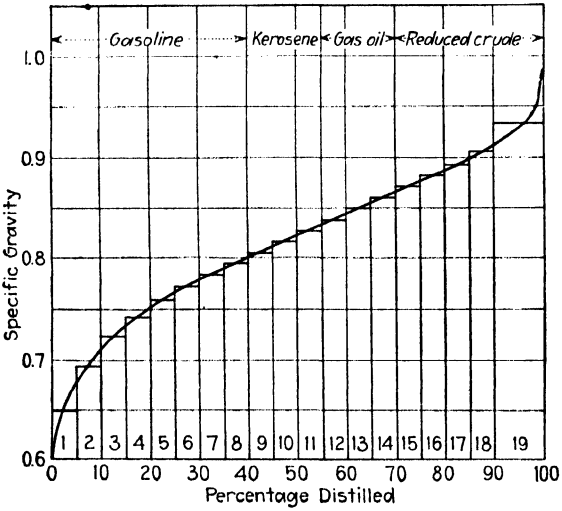

FIG. 27.—Mid per cent gravity curve.

In this example the actual fractions that were produced in the laboratory were used. In the usual case only the curve is available, and it is arbitrarily broken up into suitable fractions.

By inspecting the specific gravities computed in Example 4, it will be noted that the gravities of the kerosene and gas oil are the same as the gravities at the 47.5 per cent and the 62.5 per cent points respectively. More generally, they are the same as the gravity at the mid per cent points of these two cuts. Such might have been expected because the curve is nearly a straight line throughout these materials. Following this reasoning we may say that if the property curve is nearly a straight line between the limits of the fraction, the average property of the fraction is equal to the value of the property at the mid per cent point of the fraction, and the laborious method of integral-averaging by graphical methods, as in Example 4, need not be used except throughout sharply curving sections of the curve.

Application of Graphical Integration.—Graphical integration cannot be used in obtaining an average unless the property is an additive property. In other words, if 10 volumes of an oil of specific gravity 0.8 is mixed with 10 volumes of an oil of specific gravity 0.9, the resultant 20 volumes must have a gravity of 0.85, if the specific gravity is an additive property. Most properties are not additive. As an example, if two equal volumes of oil having different viscosities are mixed together, the resultant oil has a lower viscosity than the arithmetic (or integral) average would indicate (see blending charts, Figs. 44, 45, and 46, Chap. VIII). Although specific gravity is additive, the A.P.I. gravity is not additive because it is not a direct function of specific gravity.

The boiling-point is not an additive property because the vapor-pressures of the compounds determine the boiling-point curve and vapor-pressure is not a direct function of temperature and is not additive (see Fig. 52, page 131) unless a mol basis is used.

Property Curves.—The most important curves for engineering evaluation purposes are the true-boiling-point distillation curve (see Chap. VI), the gravity mid per cent curve, the viscosity mid per cent curves at 100 and 210°F., the viscosity yield curve, and the flash-vaporization curve. The mid per cent curves are so named because they are curves that can *usually* be integrally averaged by merely noting the mid per cent point between the limits of a fraction. However, if a sharp curvature exists at the ends of the curves, the fractions containing the curvature must be integrally averaged. Other properties, such as the flash- and fire-points and the carbon residue, are sometimes plotted as mid per cent curves, but they are not usually necessary. Figure 23 is an analysis of a paraffin-base crude oil showing these curves. These curves are dependable only when they are obtained from well-separated fractions such as those from a true-boiling-point distillation.

Gravity Mid Per Cent Curve.—This curve is obtained by plotting the gravities of the fractions of oil as shown in Fig. 27. The gravities of the fractions are plotted as a series of horizontal lines, and the curve is drawn by balancing the triangular areas against one another. Throughout its middle, the curve usually passes directly through the mid per cent point of each of the fractions because the property increases evenly, but at the ends the triangular areas must be balanced. Any point on the curve is the mid-point for any width of fraction except when the limits of the fraction include a sharply sloping portion of the curve.

Viscosity Mid Per Cent Curves.—These curves are obtained by plotting the viscosity of each fraction at the mid per cent point of the fraction. The triangular areas need not be balanced against one another as in the case of the specific-gravity mid per cent curve. There is no theoretical background for the use of these curves in this manner, but the results are accurate. Apparently the effect of the sharp curvature of these curves and the fact that viscosity is not an additive property counterbalance each other. Regardless of reasons, the curve may be used by noting the viscosity at the mid-point of the fraction. As an example, the following four (or more) fractions, each having a viscosity of 215 at 100°F., can be obtained from the oil shown in Fig. 22.

1. A 5 per cent fraction from 67.5 to 72.5 per cent.
2. A 10 per cent fraction from 65 to 75 per cent.
3. A 15 per cent fraction from 62.5 to 77.5 per cent.
4. A 20 per cent fraction from 60 to 80 per cent.

Since the curves slope steeply at higher percentages (88 to 92 per cent on curve 4, Fig. 22), they cannot be accurately read, and hence the viscosity of the residual product should be obtained from the viscosity yield curve.

Beiswenger and Child[10] by correlation with plant results have found that the pressability of a wax distillate may be estimated from the viscosity mid per cent curve at 100°F. If the upper end of a wax distillate (from a Mid-Continent crude oil) does not exceed a boiling-point of about 870°F. and the viscosity of the last drop is not over 600 at 100°F., the distillate will be pressable. With paraffin-base oils the cut-point may be somewhat higher.

[10] True Boiling Crude Analysis, Petroleum Div., Am. Chem. Soc., Atlanta Meeting (not for publication).

Viscosity Yield Curve.—This curve shows the total percentage of residual or bottom product of a given viscosity that can be produced. Since residual products are usually viscous, the viscosity yield curve is determined at 210°F. The curve indicates the integral-average viscosity of any of the many possible bottom products. The curve can be obtained by sampling the residue remaining in the flask, as various percentages of product have been collected as distillate, and determining the viscosities of these samples of bottom. However, such a method is awkward, and a simpler and sufficiently exact method is to blend the *final bottom product* (such as fraction 19, Fig. 27) with the last fractions that have been collected as distillate, to make other bottom products. This is not possible if decomposition has occurred during distillation. In order to have enough oil for the compounding of several bottom products, the final bottom and the fractions are blended in aliquot parts rather than by using all of each fraction.

Example 5. Construction of Viscosity Yield Curve.—This method applies in general to all yield curves.

Consider 19 fractions of oil obtained by a fractionating type of distillation. The properties such as gravity and viscosity of the fractions have already been recorded so that the fractions can be used in the following blends. Fractions 1 to 18 inclusive consist of 100 cc. each, and the last or bottom fraction (not distilled) amounts to 200 cc. The fractions can be blended in aliquot parts to make several bottom products as follows:

Per cent residue or bottom	Blend of fractions	Total quantity of blend, cc.
10	No. 19, 75 cc.	75
20	No. 19, 40 cc.; No. 18 and 17, 20 cc. each	80
30	No. 19, 30 cc.; No. 18, 17, 16, and 15, 15 cc. each	90
45	No. 19, 20 cc.; No. 18 to 12 incl., 10 cc. each	90
60	No. 19, 14 cc.; No. 18 to 9 incl., 7 cc. each	84

The viscosity of each blend is determined, and the four blends, along with fraction 19, constitute five points on the viscosity yield curve; also refer to Table 7, page 89.

The viscosity yield curve would not be necessary if accurate viscosity mid per cent curves could be obtained for the entire percentage range of the sample. These curves cannot extend entirely to the end of most samples because the distillation cannot be conducted to a flask temperature higher than 680°F. Even at low pressures such a temperature does not vaporize the heavy lubricating oil stocks. Furthermore, the mid per cent curves slope so sharply at the higher percentages that they cannot be accurately plotted. The viscosity yield curve is used only in the determination of the quantity of bottom product.

The several property curves tend to be confusing when plotted on a single sheet of paper (Fig. 22). For this reason the meaning of the percentage scale has been changed in plotting the viscosity yield curve. Normally the percentage scale denotes the total percentage of material that has been distilled, but for the viscosity yield curve the scale denotes the percentage of bottom product.

Often the stock contains black asphaltic material and is unsuitable as a lubricating oil stock because the removal of asphalt by treating or filtering is costly. Such stocks are evaluated by conducting a vacuum-flash vaporization which leaves a residue of solid tar. The overhead distillate is then analyzed in the true-boiling-point column, and the property curves are drawn for this heart-cut material (see page 91).

The Flash-vaporization Curve.—This curve has been discussed in Chap. VI. A method for drawing the curve empirically is presented in Chap. XIV, but the curve is so important that it should be determined experimentally. In a sense, the flash-vaporization curve is a yield curve and is often called the flash yield curve. The curve is always given at 760 mm. pressure unless the pressure is specifically stated as otherwise. A point on the curve represents the temperature at which a given amount can be vaporized or distilled if the vapor and remaining liquid are kept in equilibrium with each other until the final high temperature is attained.

A.S.T.M. End-point of Distillates.—The A.S.T.M. end-point is an important specification of such distillates as gasoline and kerosene. What is the relation of the A.S.T.M. end-point to the cut-point by a true-boiling-point distillation? No all-comprehensive relation exists because of the wide variety of different petroleum stocks. Nevertheless, Fig. 28 is an approximation that will hold in most cases. The true-boiling-point cut-point is obtained by adding a correction, in degrees Fahrenheit, to the A.S.T.M. end-point. The four curves are for different initial boiling-points. This relationship should be determined for each distillation equipment because it may vary depending upon the design and method of operation.

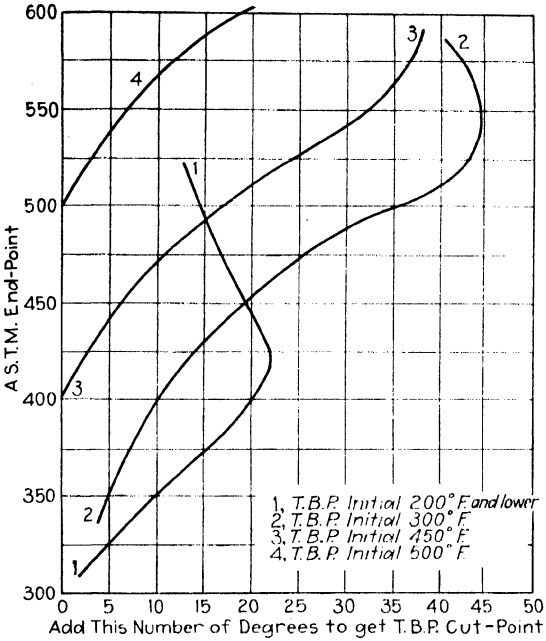

FIG. 28.—Correlation of A.S.T.M. end-point and true-boiling-point cut-point.

Example 6. A.S.T.M. End-point and T.B.P. Cut-point.—It is desired to determine the cut-point on a true-boiling-point analysis curve that will give a product having an A.S.T.M. end-point of 437°F. At an end-point of 437 (curve 1, Fig. 28) the true-boiling-point cut-point is 21° higher than the A.S.T.M. end-point. The cut-point is 437 plus 21, or 458°F. The following tabulation indicates approximate end-points as well as cut-points for other distillates:

Material	Initial boiling-point	End-point	Correction	True-boiling cut-point	Curve
Gasoline............	Less than 200	437	21	458	1
Gasoline............	Less than 200	390	18	408	1
Naphtha............	300	460	21	481	2
Kerosene............	450	530	26	556	3
Distillate............	500	590	16	606	4

Evaluation of Stocks.—The property curves that have been discussed heretofore are of general usefulness. In the following pages the necessary laboratory procedure, the construction of the curves, and the evaluations of several stocks will be discussed.

The evaluation of a *paraffin-base crude oil* is particularly simple because the oil contains no asphalt. Only a true-boiling-point distillation, conducted at first at atmospheric pressure and later at a low pressure, is necessary. Of course, the fractions from the distillation must be examined by routine tests. Table 7 is a log sheet of the data obtained in the analysis of a typical paraffin-base crude oil. Figure 29 is a graphical presentation of the data tabulated in Table 7. The vapor-temperature or true-boiling-point curve was plotted directly from the data. The gravity curve was drawn by plotting the specific gravity of each fraction as a horizontal line throughout the limits of the fraction and then drawing the curve by balancing the triangular areas against one another. The highest gravity, extending through 90 to 100 per cent, is the gravity of the residue. The viscosity mid per cent curves were drawn by plotting the viscosity

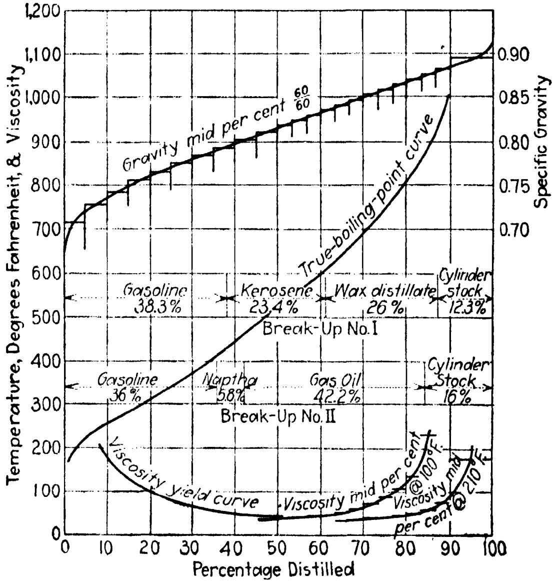

FIG. 29.—Evaluation curves from Table 7.

TABLE 7.—TRUE-BOILING-POINT ANALYSIS

Sample________________ Job No.________________

From________________ Sample No.________________

Quantity of Change—3000cc @ 60° F. A. P. I. -43.

Time	Vapor temperature at 760 mm., deg. F.	Cumulative per cent	Fraction No.	Per-cent in fraction	Sp. gr. 60/60	Viscosity		Notes
						100	210	
1. 9:06 A.M.	170	1	..	....	.....	...	....	Atmos.
2. 9:15	210	3.33						
3. 9:22	227	5	1	5	0.706			
4. 9:30	238	6.67						
5. 9:38	248	8.33						
6. 9:46	256	10	2	5	0.728			
7. 9:53	262	11.67						
8. 10:00	270	13.33						
9. 10:07	279	15	3	5	0.739			
10. 10:13	288	16.67						
11. 10:19	297	18.33						
12. 10:26	306	20	4	5	0.751			
13. 10:33	315	21.67						
14. 10:39	327	23.33						
15. 10:45	338	25	5	5	0.763			
16. 10:51	348	26.67						
17. 10:57	359	28.33						
18. 11:03	370	30	6	5	0.775			
19. 11:09	380	31.67						
20. 11:15	393	33.33						
21. 11:21	405	35	7	5	0.784			
22. 11:28	416	36.67						
23. 11:36	430	38.33						
24. 11:43	444	40	8	5	0.793	...	....	Rate slow
25. 11:51	455	41.67		....	.....	...	....	Rate slow
26. 12:01 P.M.	465	43.33						
27. 12:10	485	45	9	5	0.801			
28. 12:17	496	46.67						
29. 12:24	510	48.83						
30. 12:30	523	50	10	5	0.809	35		
31. 2:01	536	51.67						
32. 2:11	550	53.33	11	3.33	0.815	...	....	10 mm. pressure
33. 2:19	562	55						
34. 2:26	575	56.67	12	3.33	0.820			
35. 2:32	590	58.33						
36. 2:38	604	60	13	3.33	0.825	42		
37. 2:44	619	61.67						
38. 2:50	633	63.33	14	3.33	0.829			
39. 2:56	649	65						
40. 3:02	664	66.67	15	3.33	0.835	50	33	
41. 3:08	682	68.33						
42. 3:14	698	70	16	3.33	0.840	59		
43. 3:21	714	71.67						
44. 3:28	732	73.33	17	3.33	0.846	72	36.5	
45. 3:37	750	75						
46. 3:44	768	76.67	18	3.33	0.851	87		
47. 3:51	784	78.33						
48. 3:57	812	80	19	3.33	0.857	107	42	
49. 4:03	836	81.67						
50. 4:07	870	83.33	20	3.33	0.865	132	46	1 mm. pressure
51. 4:12	903	85	..	....	.....	....	....	Fast rate
52. 4:20	925	86.67	21	3.33	0.875	230	54	
53. 4:29	970	88.33						
54. 4:39	1025	90	22	3.33	0.884	...	70	Rate slow
Blend Data								
55.			23	10	0.895	...	178	Residue
56. 36cc., No. 23; 12cc., each No. 22, 21, and 20			24	20	.....	...	100	Blend
57. (21cc., No. 23; 7cc., each No. 22-17, incl.)			25	30	.....	...	62	Blend
58. (15cc., No. 23; 5cc., each No. 22-11, incl.)			26	50	.....	...	42	Blend

of each of the fractions at the mid per cent points of the fractions. The highest viscosity on the 210°F. curve is the viscosity of the bottom. The viscosity yield curve was plotted directly from the blend data given in Table 7 with the final bottom from the distillation as the 10 per cent bottom product.

Example 7. Evaluation of Paraffin-base Crude Oil.—The following sets of yields of raw stocks can be computed from the property curves of Fig. 29:

Raw stocks	Per cent	Sp. gr.	A.P.I.	Notes
Break-up 1:				
(1) 409 E.P. gasoline..	38.3	0.753	56.4	430°F. cut-point
(2) 42 A.P.I. kerosene.	23.4	0.815	42	Mid-point 50 per cent
(3) 85 Visc. at 100 wax distillate*..........	26.0	0.859	33.2	Mid-point 74.7
(4) 150 Visc. at 210 cyl. stock..............	12.3	0.892	27.1	Visc. yield curve
Break-up 2:				
(1) 391 E.P. gasoline..	36.0	0.751	56.9	410°F. cut-point
(2) 450 E.P. naphtha.	5.8	0.795	46.3	458°F. cut-point
(3) Gas oil (by difference)..............	42.2	0.837	37.4	Mid-point 62.9 per cent
(4) 120 Visc. at 210 cyl. stock..........	16.0	0.89	27.5	Visc. yield curve

* Will not be a pressable stock unless some of the heavy material is removed.

In obtaining break-up 1 the percentage of 409°F. end-point gasoline was obtained by referring to Fig. 28 which indicates that the true-boiling-point cut-point is 21°F. higher than the A.S.T.M. end-point. The 42 A.P.I. kerosene was evaluated by noting that the mid per cent point of 0.815 (or 42 A.P.I.) gravity occurs at 50 per cent on the distillation curve. Since the kerosene starts at 38.3 per cent, the end-point must be at 61.7 and the total yield is 23.4 per cent. The cylinder stock of 12.3 per cent was obtained directly from the viscosity yield curve. Twenty-six per cent of material remains, and this material is the wax distillate. The gravities of the gasoline and cylinder stock were obtained by integral-averaging, but the other gravities were obtained by noting the gravity at the mid per cent points of the cut or at 50 per cent and at 74.7 per cent respectively. The mid per cent viscosity at 74.7 per cent is 85 sec. at 100°F.

Evaluation of Dark-colored Stocks for Lubricants.—The evaluation of stocks that contain asphalt demands a more elaborate laboratory procedure. Such a stock must be subjected to preliminary distillations. The stock is first reduced by a steam distillation at atmospheric pressure to approximately 26 A.P.I. (Fig. 30). The removal of gasoline and kerosene is

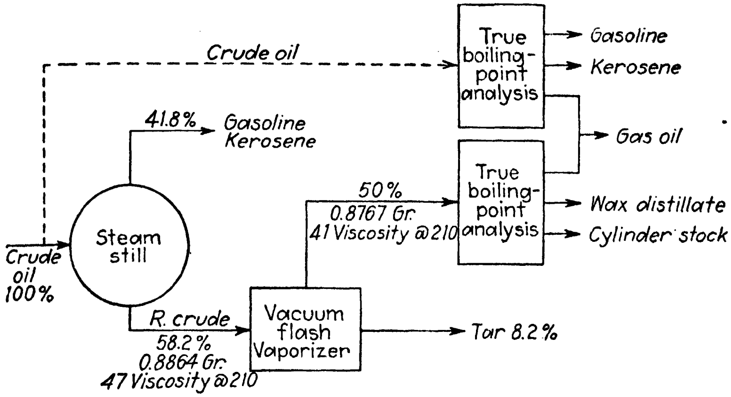

FIG. 30.—Laboratory processing scheme for evaluating heavy lubricating oil stocks.

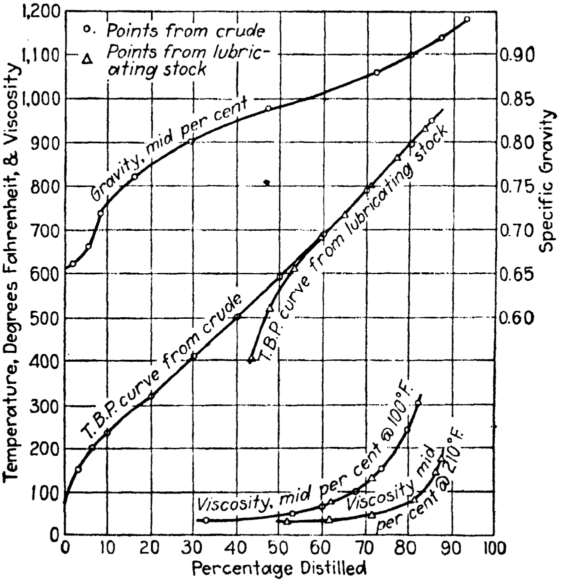

FIG. 31.—Curves for evaluating a dark-colored stock for lubricants.

necessary because these materials cannot be condensed in the subsequent vacuum-flash distillation that is necessary for the removal of tar. The reduced crude is then flashed under vacuum, distilling a clear lubricating oil stock and leaving solid tar. The lubricating oil stock can then be evaluated in the true-boiling-point apparatus. A true-boiling-point analysis of the crude oil is also necessary if the light stocks are to be evaluated.

The curves for such a laboratory procedure are given in Figs. 31 and 32. The viscosity yield curve is plotted separately (Fig. 32) because it was obtained for the heart-cut lubricating oil stock which does not contain the 8.2 per cent of tar. This viscosity yield curve (Fig. 32) is not generally useful because the plant must operate making exactly 8.2 per cent of tar bottoms or the yields will be inaccurate.

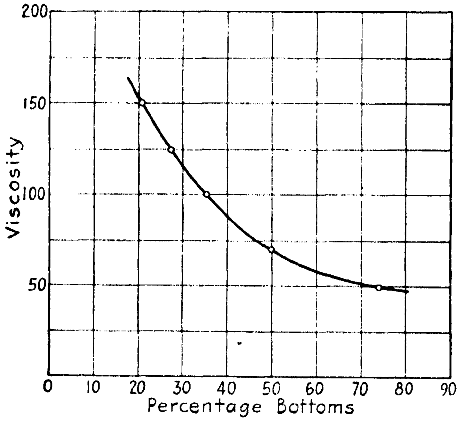

Fig. 32.—Viscosity yield curve for a heart-cut lube stock.

Dependability of Evaluation.—As an indication of the dependability of such laboratory data, consider some yields obtained from the crude oil shown in Figs. 31 and 32. Actual yields were 39.5 per cent of 69 viscosity at 100 wax distillate, 0.8654 gravity; and 10.5 per cent of 146 viscosity at 210 cylinder stock, 0.923 gravity. Computed from the curves, these yields are 40.2 per cent and 10.7 per cent respectively. Numerous other data are available, and with few exceptions the yields by these evaluation methods are as dependable as the foregoing.

The preceding method of evaluation is conducted with a minimum of decomposition, and hence the yields are the maximum that may be expected. If the designer expects to get such yields in a commercial plant, the plant must be properly designed and operated. Many poorly designed or carelessly operated plants fail to give the maximum yields, but other plants produce even larger yields than indicated by the evaluation.[11]

Many refiners are obtaining much smaller yields than those found in the preceding examples. Nevertheless, these are typical yields if the plant processing is conducted properly.[12] The destruction of lubricants by shellstill distillation is a common occurrence.

Evaluation of Other Stocks.—Most clean stocks can be evaluated by the same procedure as that outlined for paraffin-base crude oil. Stocks that can be evaluated in this manner are:

1. Light-colored crude oils.
2. Pressed distillate.
3. Wax distillate.
4. Brightstock.
5. Light-colored cylinder stocks.
6. Heart-cut lubricating oil stocks.
7. Distillates from cracking, etc.
8. Reduced crude oil for asphalt.

The viscosity curves are of little interest unless lubricating oils are to be manufactured.

In evaluating stocks for the asphalt contained in them, the same general procedure can be used but other curves are of interest. The most useful curves are the (1) specific-gravity mid per cent curve, (2) penetration yield curve, and (3) float-test yield curve. The final residue and the last fractions are blended, in determining the two yield curves.

In order to leave a solid residue, a very high vapor-temperature (about 1200°F., converted to atmospheric pressure) may be necessary. This precludes the use of the true-boiling-point type of distillation because of the big difference between the still- and vapor-temperature. A Hempel type of distillation is generally used, but even with this type of distillation the liquid temperature usually reaches about 750°F. and some decomposition occurs. If the material is not held at the high temperature for too long a time, little harm results.

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[11] The author has seen a modern vacuum plant produce 18 per cent of 200 viscosity at 210°F. brightstock, whereas only 10 per cent was previously manufactured by residual methods. This yield was 0.5 per cent more than indicated by the analysis.

[12] A Pennsylvania refiner was producing 22 per cent of a 220 viscosity at 100 viscous neutral oil from a pressed distillate by shellstill operation. The same stock yielded 45.5 per cent of the same neutral oil when processed in a steam atmospheric pipestill unit. The increase in yield came largely from the two other stocks that were being produced, so that doubtless a serious amount of decomposition had been occurring in the shellstill.

Treating and Dewaxing.—These operations are always troublesome. Most refinery laboratories have conducted hundreds of laboratory treats, but with few exceptions they do not check with plant operations. The treating of light distillates, such as pressure-still distillate and kerosene, is most successful, but even in these the color seldom checks with the color of the plant product and the losses in the laboratory are large. In the acid treating of lubricating oil stocks the results are even less satisfactory. However, by conducting a large number of treats over a period of years, it is possible to say whether or not a stock can be successfully treated in the plant, even though the laboratory and plant results do not check. Difficulty arises because the treating operation cannot be controlled and because the sludge cannot be properly separated. Usually the engineer can obtain satisfactory evaluations of the yields of raw stocks, but he must depend, to a large extent, upon plant operations for the losses during processing and for the color and properties of the finished products.

Light oils, such as gasoline and pressure distillate, are usually treated in the laboratory by placing the sample in a bottle or jug and agitating it with sulfuric acid for 10 to 20 min. The sludge is allowed to settle for several hours and is separated by decantation or by means of a separatory funnel. The settling time is sometimes shortened by centrifuging the "sour" oil for 2 or 3 min. at a speed of 1,500 r.p.m. The oil is then neutralized with caustic soda and washed with water. Treated pressure distillate must be distilled with steam or in a vacuum. The temperature is not allowed to exceed about 225°F. during the distillation. If many treats are conducted, special glass or iron stills may be built. These are usually of the batch type. An equipment for redistillation is discussed by Dailey, Meier, and Shaffer,[13] and a comparison of laboratory and plant results is given. A continuous-treating apparatus for light distillates is described by Zublin.[14]

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[13] Correlate Plant and Laboratory Procedures for Distilling Acid Treated Cracked Naphtha, *Oil Gas J.*, May 3, 1934, p. 11.

[14] Continuous Treating of Oils in the Laboratory, *Oil Gas J.*, November, 1932.

The laboratory treatment of lubricating oil stocks cannot be so easily systematized. However, Weir, Houghton, and Majewski[15] have developed a standard method of treating lubricating oil stocks. The oil is measured directly into a 100-cc. centrifuge tube, and acid is added from a small graduated pipette. The tube is stoppered and shaken either by hand or in a mechanical shaking device. The shaker can be placed in a heated cabinet if the treating is to be conducted at a high temperature. The time for shaking ranges from 10 min. for diluted samples to 40 or 60 min. for viscous oils. Next the sludge and "pepper" sludge are removed by centrifuging the tube for about one hour at 1,500 r.p.m. The sour oil is then neutralized with ammonia gas, caustic soda, or contact clay.

Most laboratories finish their lubricating oils by contact treatment with fuller's earth. Contacting is usually conducted on oils that have been treated with acid or "acid-stage" oils. About 10 per cent by weight, or less, of 200-mesh fuller's earth is mixed with the oil and heated to 450°F. for about 10 min. For neutral oils a temperature of 300° may be used. The mixture is agitated with steam or by a shaking device, and better color is obtained if the surface of the oil is protected from the air by a blanket of steam or inert gas. The clay is then filtered from the oil, while hot, by means of a Büchner funnel connected to a vacuum system.

Lubricating oil stocks are frequently diluted to allow more intimate mixing, to facilitate settling of the sludge, and to hasten filtration of the contacted oil. The material, usually naphtha, that is used as a diluent must be removed by distillation. Steam or a vacuum may be used, and the temperature should be kept as low as possible.

The dewaxing of oil in the laboratory is also a troublesome operation. A common method is to dilute the oil (about 3 to 1) and chill it in packed ice and salt to about 30° below the desired pour-point. About 1 oz. of filter-aid per 100 cc. of oil is added, and the mixture is filtered through a Büchner funnel provided with an ice-packed jacket and a cover. A vacuum is applied to the filter. A convenient method of chilling the oil is to use an ice-cream freezer. Filter leaves are also widely used. These are constructed of very fine-mesh monel-metal screen and connected to a receiver and vacuum pump. Laboratory methods of dewaxing are troublesome because filtration occurs so slowly, because a low temperature is hard to maintain, and because a low pour-point is difficult to obtain.

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[15] Control of Color of Petroleum Oils by Acid Treating, *Ref. Nat. Gaso. Mfr.*, December, 1930, p. 89.

Davis and Campbell[16] have developed a systematic method of studying wax distillate in the laboratory to determine its pressing characteristics. The examination consists of a vacuum distillation at 40 mm. pressure, a determination of the viscosity at 100°F., and an examination of the crystal formation with a microscope. Their data indicate that material boiling up to about 650°F. at 40 mm. pressure can be successfully incorporated in a wax-stock. This corresponds to a temperature of about 885°F. at 760 mm. pressure. They made a complete study of a wax distillate by analyzing it in a true-boiling-point column and examining the wax fractions and blends of them.

Evaluation of Cracking-stocks. No truly satisfactory method of estimating the yield of cracked gasoline that can be produced from a stock has been developed. In commercial operation the stock is partially cracked, and the recycle stock from it is cracked over and over again until all of the material is decomposed into gas, tar, and cracked gasoline. This cycle cannot be easily duplicated in the laboratory except by the use of a replica plant or semi-plant scale equipment. Gary and Ward[17] describe such an equipment. However, the cost of a replica plant is so great that its usefulness is generally limited to research work and the design of new cracking plants.

For mild cracking operations, such as viscosity-breaking tests or cracking for lowering the pour-point of fuel oils, bomb equipments are satisfactory. The common procedure is to heat the oil in a pressure-bomb to 820 to 860°F. for 10 to 30 min. The pressure rises as the oil is heated; and when the pressure reaches 200 lb. per square inch, a relief valve is opened a little so that the gas and some distillate can escape through a condenser. After cracking is complete, the distillate is redistilled and the material that is not in the boiling-range of gasoline is mixed with the cracked stock that remains in the bomb.

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[16] Laboratory Control of the Quality of Paraffin Distillate, *Oil Gas J.*, May 25, 1933, p. 49.

[17] A Modern Experimental Cracking Unit, *Ref. Nat. Gaso. Mfr.*, June, 1933, p. 212.

Huntington and Brown[18] have devised a bomb equipment by which dependable results can be obtained. The charge stock is introduced into a bomb that is already hot; and after the reaction is sufficiently complete, the residue can be quickly dumped by releasing the pressure and by displacement with molten solder. During the reaction the volume occupied by the stock can be accurately measured.

Corrosiveness of Stocks.—In addition to chemical methods of anaylzing the brine that is often associated with crude oil, Davis, Jones, and Neilson[19] have perfected methods for liberating hydrochloric acid and hydrogen sulfide from crude oil by distillations that simulate to some extent the heating of oil stocks in commercial equipment. The method for determining hydrochloric acid consists essentially of a steam distillation and an analysis of the gas and condensed water-solution foı acid. Hydrogen sulfide is determined in a similar manner except that the steam distillation is conducted in the presence of caustic potash.

Methods[20,21] of determining the salt content of crude oil have been developed after the method of R. R. Mathews,[22] which consists essentially in dissolving the brine from the oil into acetone and titrating with silver nitrate using a chromate indicator. Other methods are outlined by R. E. Puckett[23] and by Davis, Jones, and Neilson.[19]

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[19] Laboratory Control of the Corrosion of Distillation Equipment and of De-salting Processes, A.P.I. Eighth Midyear Meeting, Wichita, Kans., May, 24, 1938.

[20] Hawthorne and Bedell, The Removal of Inorganic Salts from Crude Petroleum, *Ref. Nat. Gaso. Mfr.*, June 1938, p. 260.

[21] U.O.P. Laboratory Test Methods for Petroleum and Its Products, Universal Oil Products Co., Chicago, 1937.

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CHAPTER VIII

PHYSICAL PROPERTIES OF PETROLEUM OIL

The discussion in Chap. IV indicated that petroleum and petroleum products are complex materials. At present the chemical and physical laws that govern the behavior of mixtures of hydrocarbons are not adequate for most calculations, and hence the engineer must base many of his computations on the average physical properties of petroleum oil cuts. It has often been necessary to resort to empirical equations of these properties for ease in correlation and to permit extrapolation to conditions for which data are lacking.

Specific Heat.—The specific heat of a material is defined as the quantity of heat required to raise the temperature of a unit weight of material through a temperature difference of one degree. Universally the oil industry uses the English system in which the specific heat is defined as the number of British thermal units (B.t.u.) required to raise the temperature of 1 lb. of oil 1°F. and is expressed as B.t.u. per pound per degree Fahrenheit.

The specific heat increases with temperature but usually not as a linear function of temperature. However, the specific heat of petroleum oils, by the information now available, is a linear function. The specific heat also depends upon the gravity of the oil so that it is a function of both temperature and gravity.

Figure 33 is a chart of the specific heats of Mid-Continent petroleum oils. The data of Fortsch and Whitman[1] and of Weir and Eaton[2] were used. The two sets of data do not agree exactly, but an average was used in constructing Fig. 33. The curves for 70 and 10 A.P.I. material are not so exact as the other curves because not many oils of these gravities were studied. The critical line indicated in Fig. 33 is not exact because the critical temperature is governed more by the boiling-range than

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[1] Specific Heats of Oils, *Ind. Eng. Chem.*, **18**, 795 (1926).

[2] Heat Content of Petroleum Oil Fractions at Elevated Temperatures, *Ind. Eng. Chem.*, **24**, 210 (1932).

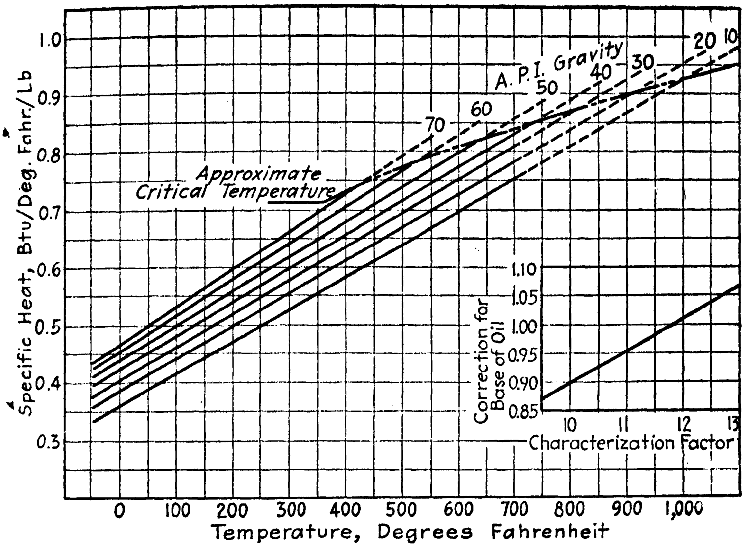

FIG. 33.—Specific heat of Mid-Continent oils (liquid).

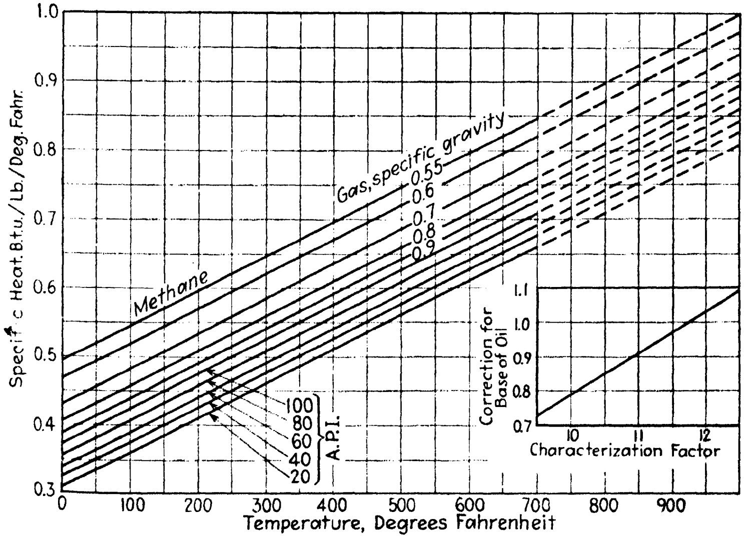

FIG. 34.—Specific heat of Mid-Continent oil vapors.

by the gravity. Nevertheless, it is included in the figure as a warning that liquids cannot exist above the critical point.

Example 8. Heat Required to Raise the Temperature of Oil.—How much heat is required to raise the temperature of 1,000 lb. of a 40 A.P.I. mixed-base oil from 100 to 600°F.?

$$\begin{aligned} \text{Specific heat at } 100 &= 0.48 \\ \text{Specific heat at } 600 &= \underline{0.775} \\ &\ 1.255 \end{aligned}$$

$$\text{Average specific heat from 100 to 600} = \frac{1.255}{2} = 0.627$$

$$\text{Also note the specific heat at 350} = 0.627$$

$$1{,}000\ (600 - 100)\ 0.627 = 313{,}500 \text{ B.t.u.}$$

The data of Bahlke and Kay[3] for petroleum vapors from Mid-Continent oils are presented in Fig. 34. Data on vapors are not extensive, but specific heats can be obtained from Weir and Eaton's[2] data. From their data the specific heats are slightly higher than those shown in Fig. 34, but they check remarkably well. The specific heats of gases are taken from the excellent summary of the properties of oils presented by Egloff, Nelson, Watson, *et al.*[4] before the World Petroleum Congress in 1936.

The characterization factor[4] found to be so useful in cataloguing crude oils (Chap. VII) is of even greater value in accounting for the degree of paraffinicity of individual fractions.

$$K = \frac{\sqrt[3]{T_B}}{s}$$

where K = U.O.P. characterization factor.

T_B = average boiling point, deg. R. = deg. F. + 460.

s = specific gravity at 60°F.

The factor has been useful in correlating many properties, among which are hydrogen content, aniline point, thermal expansion, and Viscosity Index, as well as the relationships that are employed in this chapter. Correction factors[4] for the effect of base of oil on specific heat are included on Figs. 33 and 34.

Characterization Factor.—In addition to the relation of this factor to the cube root of the boiling-point, its relation to gravity, molecular weight, critical temperature, and viscosity is found to be particularly useful because it permits a joint comparison of all properties. The relation[4] among these several variables is given in Figs. 35 and 36. The use of the 50 per cent boiling-point rather than the molal average boiling-point is not entirely accurate, but for most design work it is adequate.[4] Furthermore, the distillation curve for high-boiling materials is seldom available or complete, and hence the 50 per cent boiling-point will be used.

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[3] *Ind. Eng. Chem.*, **21**, 942 (1929).

[4] The Modern Cracking Process, *Oil Gas J.*, July 2, 1936, p. 34.

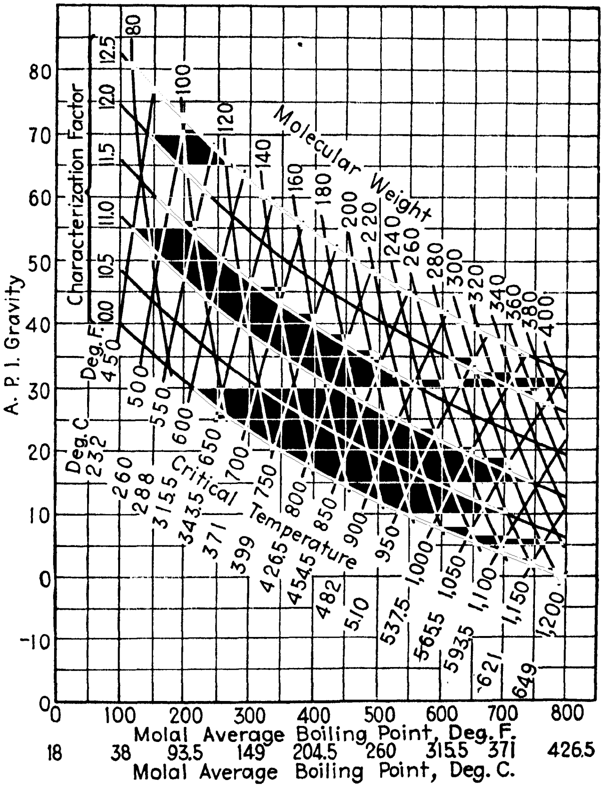

FIG. 35.—Molecular weights, critical temperatures, and characterization factors of petroleum fractions related to characterization factor. (*Courtesy of Oil and Gas Journal.*)

Example 9. Use of Characterization Factor Relationships.—An oil that has an average boiling-point of 500°F. and a gravity of 31.5 A.P.I. will have, according to Fig. 35, a characterization factor of about 11.35 and would be classed as a Gulf Coast stock. Other data are:

Molecular weight	202 (Fig. 35)
Critical temperature	854°F. (Fig. 35)
Viscosity (centistokes)	1.1 (Fig. 36)

It should be noted that if the values of any two of the properties mentioned are known, the values of the other properties can be determined.

Latent Heat.—The heat of vaporization, commonly referred to as the latent heat, is usually defined as the B.t.u. required to vaporize 1 lb. of a liquid at its atmospheric boiling-point. If vaporization takes place at another pressure (or temperature), the latent heat should be specified as such. The latent heat varies with the temperature (or pressure) at which vaporization occurs and with the type of hydrocarbon.

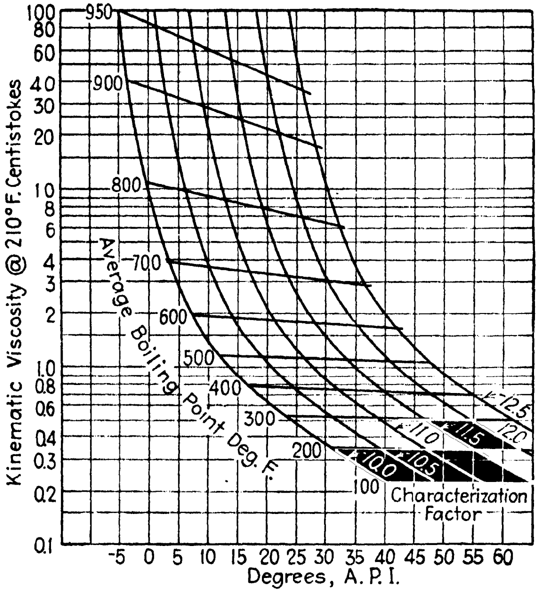

FIG. 36.—Relation of viscosity to characterization factor. (*Courtesy of Oil and Gas Journal.*)

The latent heats[4] at atmospheric pressure for petroleum fractions are given in Fig. 37 as a function of boiling-point and molecular weight or characterization factor. At other pressures (and temperatures) the data on latent heat are not extensive, and

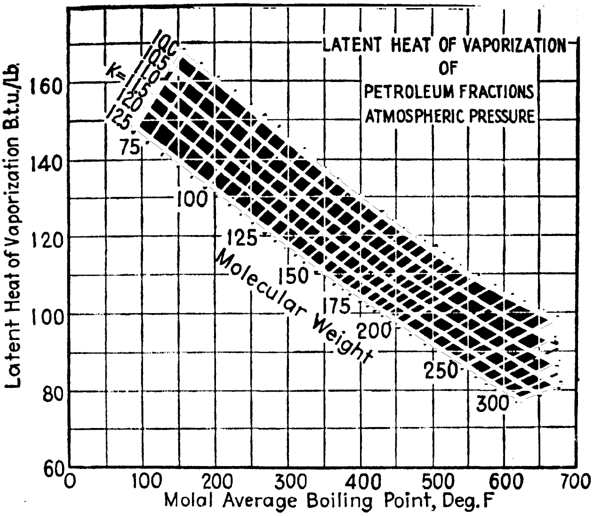

FIG. 37.—Latent heat of vaporization of petroleum fractions at atmospheric boiling-point. (*Courtesy of Oil and Gas Journal.*)

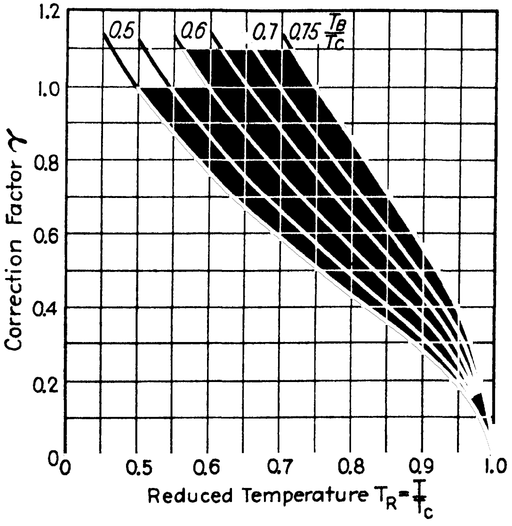

FIG. 38.—Temperature correction to heat of vaporization. (*Courtesy of Oil and Gas Journal.*)

hence a general method such as that outlined by Watson[5] must be employed. The latent heat at any temperature is described in terms of the latent heat at the normal boiling-point, as follows:

$$L = \gamma L_B \frac{T}{T_B} \tag{3}$$

where L = heat of vaporization at absolute temperature T.

L_B = heat of vaporization at absolute normal boiling-point T_B.

γ = a factor obtained from Fig. 38.

The reduced temperature term used in Fig. 38 is explained on page 111 of this chapter.

The latent heat decreases with temperature until it has a value of zero at the critical temperature. Furthermore, the critical temperatures of high A.P.I. materials are lower than for low A.P.I. materials, and hence the latent-heat curves, when plotted as functions of gravity and temperature, should cross one another at some point.

Example 10. Latent Heat.—A mixed-base, narrow boiling-range fraction has a gravity of 35 A.P.I. The latent heat of this fraction at atmospheric pressure and also at 500°F. is desired.

A mixed-base stock will have a characterization factor of about 11.9 (see page 77). The following properties were read from Fig. 35.

Atmospheric boiling-point	580°F. (1040°R.)
Molecular weight	255
Critical temperature	900°F. (1360°R.)

From these data, the latent heat at atmospheric pressure is found to be about 88 by reference to Fig. 37.

In order to estimate the latent heat at 500°F., additional factors must be set down;

$$\frac{T_B}{T_C} = \frac{1040}{1360} = 0.765$$

$$T_R = \frac{T}{T_C} = \frac{500 + 460}{1360} = 0.706$$

γ from Fig. 38 = about 1.16

The latent heat at 500°F. from Eq. (3) is

$$L = 1.16 \times 88 \times {}^{960}\!/\!_{1040} = 94$$

The average boiling-point of mixtures is defined with difficulty. An arithmetic average, from the distillation curve, does not completely describe the vaporization properties because the vapor-pressure is not directly proportional to temperature. A logical average boiling-point is the 100 per cent point on the flash-vaporization curve because the material cannot be completely vaporized at any lower temperature. For batch distillation the arithmetic average temperature should be used for computing the latent heat, but for continuous distillation, as in a pipestill, the 100 per cent point on the flash-vaporization curve should be used. The temperature at the 100 per cent point on the flash-vaporization curve is approximately the same as the temperature at the 70 per cent point of the material on the true-boiling-point curve. For some other purposes, such as estimating the molecular weight, gravity, or viscosity, the 50 per cent boiling-point should be used.

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[5] The Prediction of Critical Temperatures and Heats of Vaporization, *Ind. Eng. Chem.*, **23**, 360 (1931).

The heat of fusion of paraffin wax as reported by various experimenters ranges from 63 to 78.5 B.t.u. per pound, and perhaps the best data indicate 72.5.

Effect of Pressure on Heat Content.—A relatively simple method of correcting the heat content, or enthalpy, of gases or vapors for the effect of pressure is also proposed by Watson and Nelson.[4] The enthalpy or total heat at atmospheric pressure may be computed, then a correction factor from Fig. 39 is applied. The correction (ΔH) applies for vapors heated through the temperature range of 60°F. to temperature T. The symbol ΔH refers to the correction in B.t.u. per pound; T refers to temperatures in degrees Fahrenheit absolute; and M refers to molecular weight.

Total heats at atmospheric pressure can be computed by determining the heat required to heat a pound of liquid to its atmospheric boiling-point, vaporizing the liquid at atmospheric pressure, and heating the vapor to the final high temperature using the specific heats for vapors. The errors in such a computation are usually negligible; but if the pressure differs greatly from atmospheric pressure, a correction should be made using Fig. 39 as outlined in Example 11.

Various total heat equations and charts have been proposed; but until more complete data are available, their accuracy will be in question. In special instances the preparation of enthalpy charts by the use of Fig. 39 may be justified. The effect of pressure on the specific heat of liquids is negligible except at temperatures close to the critical-point.

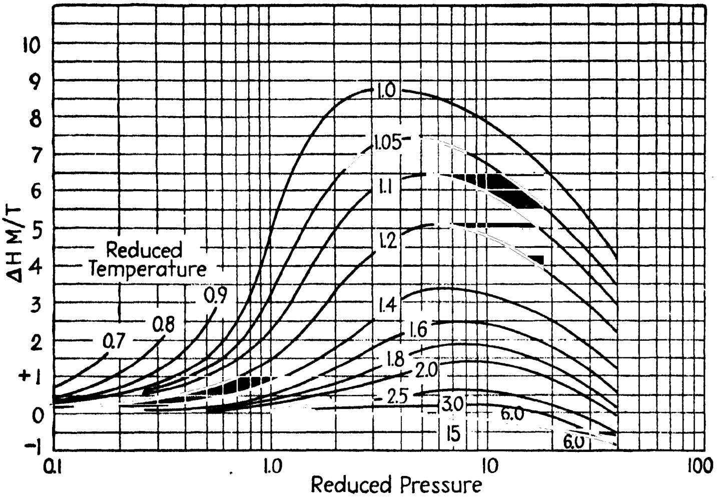

FIG. 39.—Correction of total heat content (enthalpy) for pressure. (*Oil Gas J.*)

Example 11. Total Heat at Elevated Pressures.—A 60 A.P.I. Pennsylvania gasoline at 60°F. is to be heated, vaporized, and superheated to 500°F. at an absolute pressure of 200 lb. per sq. in. How much heat is required per pound of gasoline?

General properties of the gasoline, taken from Fig. 35, are

Average boiling-point	290°F. (750°R.)
Critical temperature	610°F. (1070°R.)
Molecular weight	128

Correction factors (Figs. 33, 34) for the specific heats to account for the paraffinicity of the stock are 1.04 for liquids and 1.09 for vapors.

The total heat at atmospheric pressure is

Heat of liquid (Fig. 33)	$1(290 - 60)0.565 \times 1.04$	= 135
Latent heat (Fig. 37)	1×121	= 121
Heat of vapor (Fig. 34)	$1(500 - 290)0.54 \times 1.09$	= 124
Total heat, B.t.u. per lb		= 380

In order to apply a correction for pressure, reduced temperatures and pressures must be determined.

Critical pressure (Fig. 42) = 340 lb. per sq. in.

$$P_R = \frac{P}{P_C} = \frac{200}{340} = 0.588$$

$$T_R = \frac{T}{T_C} = \frac{500 + 460}{1070} = 0.898$$

From these data, the value of $\Delta HM/T$ is found (Fig. 39) to be about 3.4, and the correction for pressure is

$$\Delta H = \frac{3.4 \times 960}{128} = 25.5 \text{ B.t.u. per lb.}$$

Thus, the total heat at 500°F. at 200 lb. per sq. in. is 380 − 25.5 = 354.5 B.t.u. per lb. of gasoline.

Specific Volume.—The volume occupied by 1 lb. of vapor is called the specific volume. According to the laws governing the behavior of perfect gases, the volume varies inversely as the pressure (Boyle's law) and directly as the absolute temperature (Gay-Lussac's or Charles's law) or

$$\frac{PV}{T} = \frac{P'V'}{T'} = R \text{ (the gas-law constant)} \tag{4}$$

where P and P' = lb. per sq. in. abs. (14.7 + gage pressure).
V and V' = volume, cu. ft.
T and T' = absolute temperature or (deg. F. + 460).
R = 10.7 when considering 1 lb.-mol of gas.

At standard conditions of 32°F. and a pressure of 1 atm. or 760 mm., the volume of 1 lb.-mol of a perfect gas is 359 cu. ft. At 60°F. and 760 mm. the volume is 379.4 cu. ft. (379 is commonly used).

The volume of 1 lb.-mol of a perfect gas, *viz.*, 359 cu. ft., is the factor that relates the volume of a gas to its weight. The foregoing laws are sufficiently exact for engineering calculations involving such gases as air, nitrogen, oxygen, flue gas, and natural gas, unless the pressure exceeds about 200 lb. per square inch. For high pressures and for the vapors handled in the refinery the laws are not exact but they are used extensively.

Example 12. Volume of Flue Gas.—A flue gas consisting of N_2, O_2, CO_2, and water vapor has a molecular weight of 30. What is the volume of 100 lb. of this gas at 200°F. and a barometric pressure of 740 mm.?

$$\text{Volume at 200°F.} = \frac{100}{30} \times 379 \times \frac{760}{740} \times \frac{(460 + 200)}{(460 + 60)} = 1{,}648 \text{ cu. ft.}$$

What is the volume of 100 lb. at 1000°F. and 10 lb. per sq. in. gage?

$$\text{Volume at 1000°F.} = \frac{100}{30} \times 379 \times \frac{14.7}{24.7} \frac{(460 + 1{,}000)}{(460 + 60)} = 2{,}110 \text{ cu. ft.}$$

also

$$\text{Volume} = \frac{100}{30} \times \frac{10.7 \times 1{,}460}{24.7} = 2{,}110$$

Pressure-volume-temperature Relations of Vapors.—Petroleum vapors do not follow the gas laws. In general, low-molecular-weight vapors such as natural gasoline and gasoline vapors may be handled as perfect gases up to gage pressures of 35 lb.

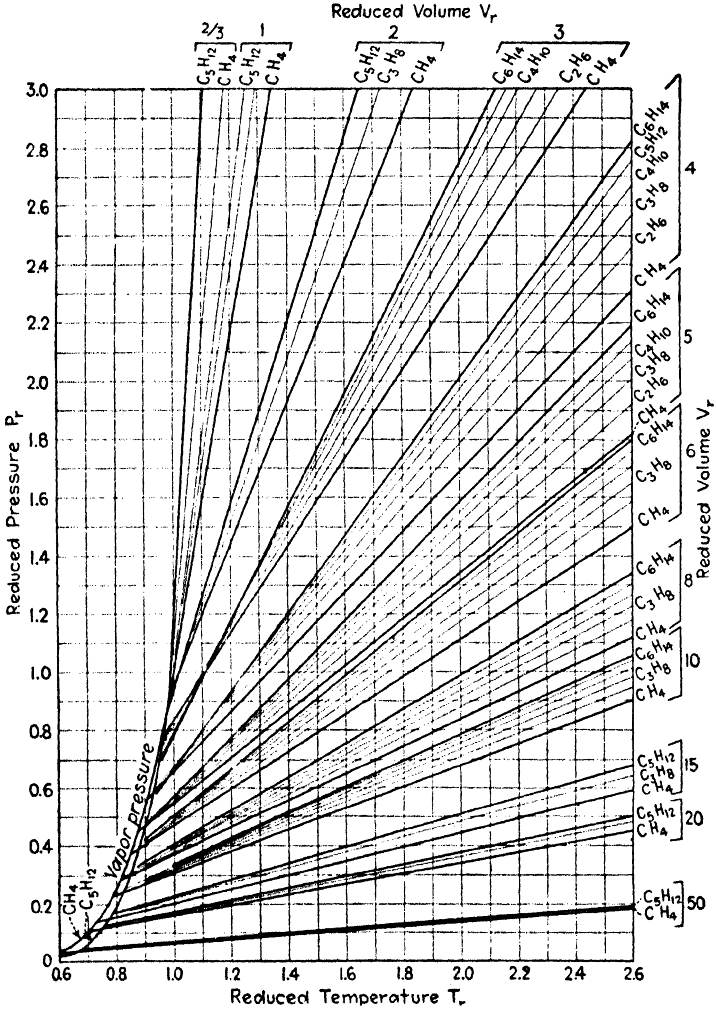

FIG. 40.—Relation of pressure, volume, and temperature for the normal paraffin hydrocarbons. (*Dr. G. G. Brown and Ind. Eng. Chem.*)

ular-weight vapors such as natural gasoline and gasoline vapors may be handled as perfect gases up to gage pressures of 35 lb.

per square inch without introducing great errors. For heavier vapors the laws are not exact, but they are widely used because no other convenient laws are available. However, Dr. G. G. Brown[6] of the University of Michigan has studied the behavior of the normal paraffin hydrocarbons. His correlation is given in Fig. 40, and similar information, given in Fig. 41, was taken from Watson *et al.*[7] This figure was prepared for all gases, and the present state of knowledge concerning the compressibility of gases does not warrant closer discrimination.

The theorem of corresponding states[6] affords a method of correlating the scattered data. This theorem postulates that all similar substances have corresponding volumes at corresponding temperatures and pressures, if the reference point of correspondence is the critical-point. Thus, instead of using pressure, volume, and temperature directly, the ratio of each of these to their value at the critical-point is used. These ratios are called reduced pressures, temperatures, or volumes.

$$V_R = \text{reduced volume} = \frac{\text{volume at a specified condition}}{\text{volume at critical-point}} = \frac{V}{V_c}$$

$$T_R = \text{reduced temperature} = \frac{\text{absolute temperature}}{\text{absolute critical temperature}} = \frac{T}{T_c}$$

$$P_R = \text{reduced pressure} = \frac{\text{absolute pressure}}{\text{absolute critical pressure}} = \frac{P}{P_c}$$

Tables 8 and 9 give critical data by which reduced conditions can be computed. Most of the data were taken from "Physical Constants of the Principal Hydrocarbons" by the technical staff of The Texas Company.

The relation of reduced temperatures, pressures, and volumes is given in Fig. 40. The same relations may be handled more conveniently, for most computations, by means of the compressibility factor Z. Perfect gases behave as follows:

$$PV = nRT \text{ (ideal)}$$

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[6] BROWN, SOUDERS, and SMITH, Pressure-volume-temperature Relations . . . , *Ind. Eng. Chem.*, **24**, 513 (1932).

[7] HOUGEN and WATSON, "Industrial Chemical Calculations," 2d ed., p. 398, John Wiley & Sons, Inc., New York, 1936; and DODGE, B. F., *Ind. Eng. Chem.*, **24**, 1353 (1932).

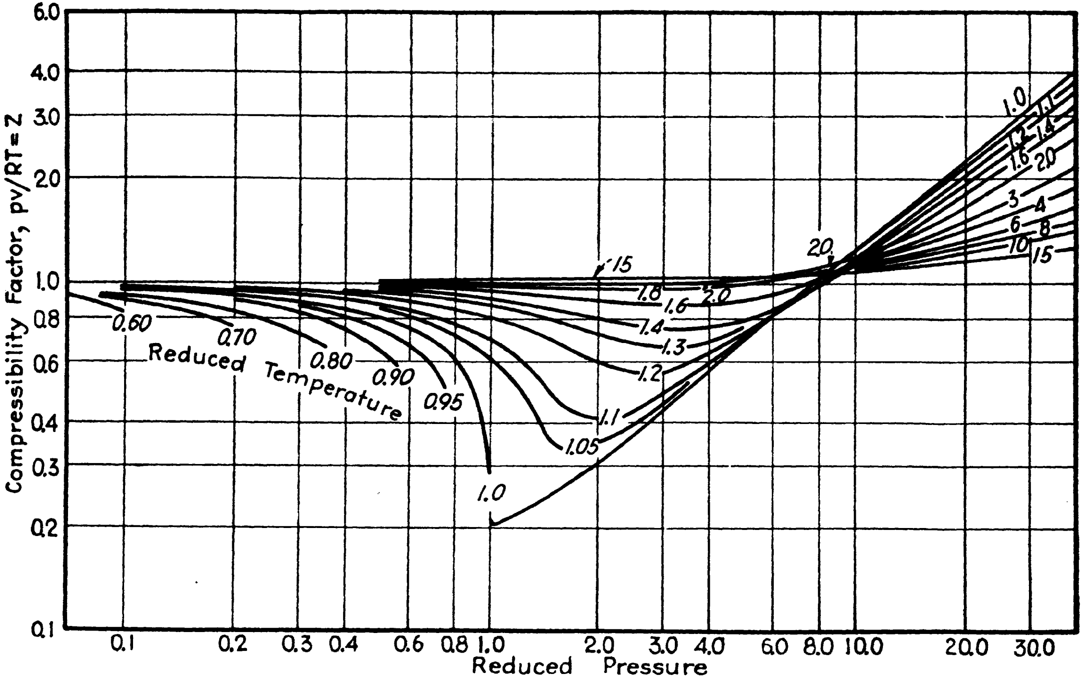

Fig. 41.—Compressibility factors of gases and vapors. (*Courtesy of "Industrial Chemical Calculations," John Wiley & Sons, Inc., New York.*)

R = gas constant = 10.7 for the following units: 1 mol of gas, volume, cu. ft.; pressure, lb. per sq. in. abs.; and temperature, deg. F. abs.
n = number of mols of gas.

Other gases deviate from the foregoing by the factor Z:

$$PV = ZnRT \tag{5}$$

Values of Z may be obtained from Fig. 41.

Example 13. Pressure-volume-temperature Relations of Gases That Are Not Ideal.—*A*. One-pound-mol of C_3H_8 (44 lb.) is held in a container having a capacity of 31.2 cu. ft. The temperature is 280°F. What is the pressure? (See Table 8.)

$$T_c = 665\text{°F. abs.}$$
$$P_c = 616 \text{ lb. per sq. in.}$$
$$V_c = 3.12 \text{ cu. ft.}$$
$$T_R = \frac{460 + 280}{665} = 1.113$$
$$V_R = \frac{31.2}{3.12} = 10$$

By Fig. 40 the reduced pressure = 0.372.

$$P_R = 0.372 = \frac{P}{616}$$
$$P = 229 \text{ lb. abs.}$$

As a check, the original volume can be computed from Fig. 41.

$$P_R = 0.372$$
$$Z = \text{approximately } 0.905$$
$$PV = ZnRT$$
$$V = \frac{0.905 \times 1 \times 10.7 \times 740}{229} = 31.2 \text{ cu. ft.}$$

By the gas laws the computed pressure would be

$$P = \frac{1 \times 10.7 \times 740}{31.2} = 254 \text{ lb. abs.}$$

B. One thousand cubic feet of methane is to be compressed from 60°F. and atmospheric pressure to 500 lb. per sq. in. gage and a temperature of 50°F. What volume will it occupy at these conditions?

$$\text{Mols } CH_4 = \frac{1{,}000}{379} = 2.64$$

At final conditions,

$$T_R = \frac{460 + 50}{344} = 1.48$$
$$P_R = \frac{500 + 14.7}{673} = 0.765$$

TABLE 8.—PROPERTIES OF PARAFFIN HYDROCARBONS*

	Methane	Ethane	Propane	i-Butane	Butane	i-Pentane	Pentane	Hexane	Heptane	Octane
Molecular weight	16.03	30.05	44.06	58.08	58.08	72.09	72.09	86.11	100.13	114.14
Specific gravity, liquid 60/60	0.300	0.3738	0.5089	0.5665	0.5824	0.6241	0.6306	0.6633	0.68372	0.70279
Specific gravity, vapor, to air	0.559	1.037	1.5206	2.0042	2.0042	2.494	2.491	2.975	3.459	
Boiling-point, deg. F	−257	−127.5	−44	13.5	31	82	97	156	209	258
Critical temp., deg. R	344	549	665	733	765	829	846	914	976	1022
Critical pressure, lb. per sq. in. abs.	673	715	616	543	550	483	484	440	405	370
Critical volume, cu. ft. per lb.-mol.	1.59	2.29	3.12	....	4.14	4.93	4.97	5.88	6.85	7.86
Specific heat, vapor	$0.543^{15.5}$	$0.410^{15.5}$	0.473^{15}	0.462^{15}	0.459^{15}	0.471^{100}	0.409^{86}			
Specific heat, liquid at 60°F	....	....	0.6	0.63	0.58	0.53	0.54^{17}	0.531^{22}	$0.53^{26.2}$	0.526^{25}
Ratio of specific heats at 60°F	1.274	1.22	1.15	1.11	....	....	1.08^{86}	1.08^{80}		
Latent heat, B.t.u. per lb. at B.P.	220	199	183	151	165	160	154	144	137	128
Coefficient of expansion	$0.003681^{0\text{-}100}$	$0.003750^{0\text{-}100}$	$0.003240^{0\text{-}37.7}$	$0.002304^{10\text{-}37.7}$	$0.002034^{10\text{-}37.7}$	$0.001546^{5\text{-}10}$	$0.00154^{0\text{-}30}$	$0.00135^{0\text{-}30}$	0.001222	$0.00116^{0\text{-}80}$
Inflammability limit:										
Low, per cent in air	5.3	3.2	2.4	1.9	1.9	....	1.45	1.3	1.1	
High, per cent in air	14.0	12.5	9.5	8.5	8.5	....	7.5			
Heat of combustion, gross, kg.-cal. per mol at constant pressure	212.79	372.8	530.57	686.3	687.94	838.00	845.27	1002.4	1159.4	1316.4
Octane No., motor method	125	125	125	99	91	90	64	59	0	−28

* The numbers above some of the data are temperatures in deg. C. at which the data are applicable.

TABLE 9.—PROPERTIES OF VARIOUS HYDROCARBONS

	Ethene	Propene	i-Butene	Butene-1	Cyclo-hexane	Benzene	Toluene
Molecular weight	28	42	56.1	56.1	84.1	78	92.1
Specific gravity, liquid	0.5699^{-104}	0.6095^{-48}	0.6268^{-6}	0.625^{-6}	0.7785	0.87366^{25}	0.86697
Specific gravity, vapor, to air	0.9852	1.469	2.011	1.96			
Boiling-point, deg. F	−155	−53.7	20	21	178	176	232
Critical temperature, deg. R	510	657	762	751	996	1010	1068
Critical pressure, lb. per sq. in. abs	748	660	......	......	585	703	611
Critical volume, cu. ft. per lb. mol	2.04	......	......	......	4.93	4.1	5.05
Specific heat, vapor	0.365^{18}	$0.371^{15.5}$	$0.362^{15.5}$	$0.362^{15.5}$	$0.440^{25.9}$	0.414^{27}	0.398^{30}
Latent heat, B.t.u. per lb. at B.P	225	197	167	173	155	170	155.5
Coefficient of expansion	$0.006894^{-17.8-10}$	$0.002718^{-17.8-10}$	$0.001872^{-17.8-10}$	$0.001908^{-17.3-10}$	0.00120^{0-30}	0.001215^{0-30}	0.00106^{0-30}
Heat of combustion, gross, kg.-cal. per mol at constant pressure	337.28	491.82	647.2	649.66	940.0	782.0	934.2
Octane No., motor method	......	......	87	80	87	97	100+

From Fig. 41

$$Z = 0.925$$

$$PV = ZnRT$$

$$V = \frac{0.925 \times 2.64 \times 10.7 \times 510}{514.7} = 25.9 \text{ cu. ft.}$$

By the gas laws the volume is 28.1 cu. ft.

The Critical-point.—When a compound is heated at atmospheric pressure, it eventually reaches its boiling-point and is completely vaporized at a constant temperature unless the pressure is increased. If the pressure is increased, the compound is completely condensed and cannot be vaporized again unless the temperature is also increased. This mechanism, alternately increasing the pressure and temperature, functions until at some high temperature and pressure it is found that the material cannot be condensed regardless of the amount of pressure applied. This point is called the critical-point, and the temperature and pressure at the critical-point are called the critical temperature and pressure respectively. The liquid-phase and

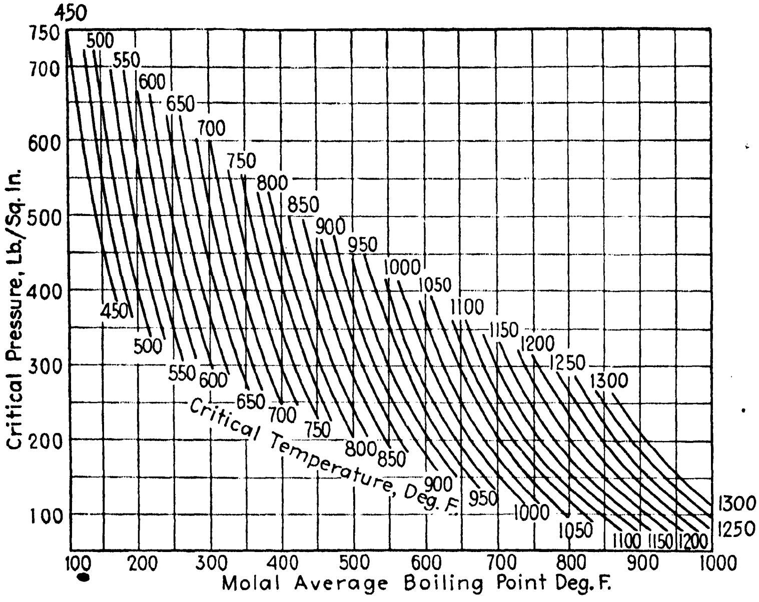

FIG. 42.—Critical pressures of the hydrocarbons. (*Courtesy of Oil and Gas Journal.*)

vapor-phase merge at the critical-point so that one phase cannot be distinguished from the other. No volume change occurs when a liquid is vaporized at the critical-point, and no heat is required for vaporization, but the coefficient of expansion has become large (Fig. 43, page 119).

The critical temperatures and pressures of some pure compounds are given in Tables 8 and 9. In addition, Figs. 35 and 42 may be used to estimate the critical temperatures and pressures of higher boiling hydrocarbons or narrow boiling-range fractions.

Insufficient information concerning the behavior of mixtures requires that the pseudo critical temperature and pseudo critical pressure be used for most oil mixtures. The pseudo critical-point as developed by W. B. Kay[8] may be defined as the molal average critical temperature and pressure of the several materials that constitute a mixture. It may be used as the critical-point of a mixture in computing reduced temperatures, pressures, etc. However, in computing the pressure-volume-temperature relations of mixtures by use of the pseudo critical-point, it must be borne in mind that the values are not accurate in the region of the critical-point—and that it cannot be applied to mixtures of gas and liquid (refer to page 247).

Example 14. Pseudo Critical-point.—Critical values for ethane and propane are:

	Ethane	Propane
Critical temperature, deg. R.	549	665
Critical pressure	715	616

For a 90 mol per cent propane mixture of these gases:

Pseudo critical temperature....... $(0.1 \times 549) + (0.9 \times 665) = 653.4°\text{R}.$

Pseudo critical pressure........... $(0.1 \times 715) + (0.9 \times 616) = 625.9$

These values may be used to compute volumes, pressures, etc., of such a mixture.

Coefficient of Expansion.—Government bulletins[9] present volume-correction tables for (1) straight-run products (10 to

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[8] Density of Hydrocarbon Gases and Vapors, *Ind. Eng. Chem.*, **28**, 1014 (1936).

[9] *Natl. Bur. Standards Misc. Pub.* 97; *Nat. Bur. Standards Circ.* 154 and its supplement; *Nat. Bur. Standards Tech. Paper* 77.

95 A.P.I.), (2) volatile products (95 to 150 A.P.I.), (3) asphalt and fluxes (0 to 15 A.P.I.), (4) mixtures of gasoline and benzol (0–50 per cent), and (5) cracked gasoline. The mean coefficients of expansion for different gravity materials are approximately as follows:

Gravity Range	Mean Coefficient of Expansion
79 and lighter	0.0008
78.9–65.0	0.0007
64.9–51.0	0.0006
50.9–35.0	0.0005
34.9–15.0	0.0004
14.9–0	0.00036

The coefficient of expansion may be defined as the fraction of unit volume that a unit of material will expand if it is heated through one degree.

Example 15. Coefficient of Expansion and Fig. 43.—One barrel of a 19 A.P.I. oil is to be heated from 60 to 400°F. What volume will it occupy?

Coefficient of expansion = 0.0004 approximately
Increase in volume = 1(400 − 60).0004 = 0.136 bbl.
Total volume = 1.136 bbl.

Using Fig. 43,

Sp. gr. at 60°F. (19 A.P.I.) = 0.9402

Follow 0.94 line to 400°F.

Sp. gr. at 400°F. = 0.83

$$\text{Volume at } 400°\text{F.} = 1 \times \frac{0.94}{0.83} = 1.13 \text{ bbl.}$$

The volume by Fig. 43 is probably the more accurate.

Density and Specific Gravity.—The density of petroleum products at elevated temperatures[10] can be obtained from Fig. 43 (see Example 15). The figure relates the specific gravity at 60°F. with the specific gravity at other temperatures. The number accompanying each line indicates the gravity of the material at 60°F.

Density is defined as weight per unit of volume. In the petroleum industry, density is usually expressed as pounds per gallon. Since 1 gal. of water at 60°F. weighs 8.328 lb., the density is

$$\text{Density, lb. per gal.} = \text{sp. gr.} \times 8.328$$

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[10] NELSON, W. L., Determining Densities . . . at High Temperatures, *Oil Gas J.*, Jan. 27, 1938, p. 184.

Viscosity of Blends.—Viscosity is not an additive property. When one volume of a 500 viscosity oil is mixed with one volume of a 100 viscosity oil of the same base, the resultant mixture has a viscosity of 209 rather than 300. When oils of a different base are mixed, the deviation is even greater. Figures 44, 45, and 46 were published by O. G. Wilson[12] and are perhaps the most convenient charts that have been published. The A.S.T.M.[13] has

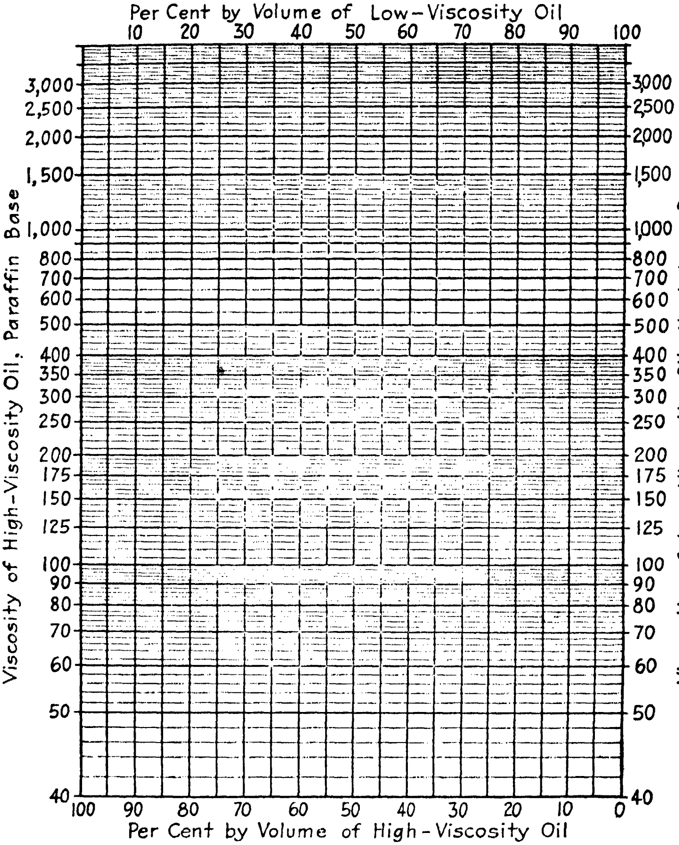

FIG. 45.—Viscosity blending chart. High-viscosity paraffin oil and low-viscosity naphthene oil. (*O. G. Wilson, Nat. Petroleum News.*)

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[12] Chart Method of Predicting Viscosity, *Nat. Petroleum News*, May 22, 1929, p. 87.

[13] Committee D-2, Petroleum Products and Lubricants, A.S.T.M., 260 South Broad Street, Philadelphia, Pa.

recently adopted standard viscosity temperature charts (D341-39) which can be used both for the change of viscosity with temperature and for determining the proportions for blends. Viscosity values at two temperatures must be available for each oil in order to use the charts.

Figure 44 is for oils of the same base.

Figure 45 is for high-viscosity paraffin oils and lower viscosity naphthene oils.

Figure 46 is for high-viscosity naphthene oils and lower viscosity paraffin oils.

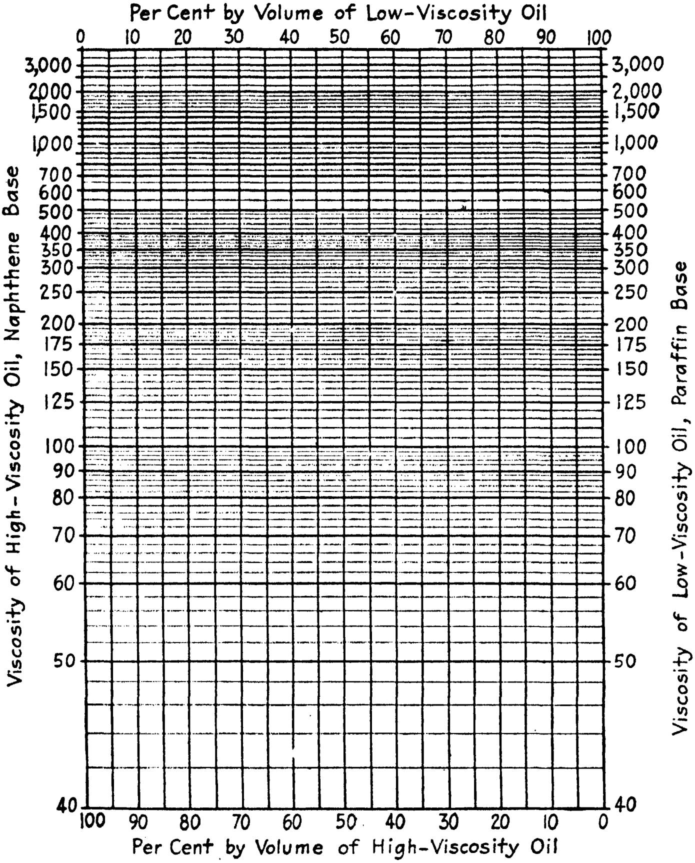

FIG. 46.—Viscosity blending chart. High-viscosity naphthene oil and low-viscosity paraffin oil. (*O. G. Wilson, Nat. Petroleum News.*)

The viscosity of the high-viscosity oil is used on the left axis of the charts and of the lower viscosity oil on the right axis.

Example 17. Blending Lubricating Oils.—It is desired to produce an S.A.E. 30 (lowest viscosity 384) motor oil by blending 600 viscosity at 100 paraffin stock and 200 viscosity at 100 naphthene stock. In what proportions should they be mixed? (Refer to Fig. 45.)

A straight line is drawn across the chart from 600 on the left to 200 on the right. This line intersects the 384 viscosity line at about 40 per cent of low-viscosity oil. (Read at top.)

Change of Viscosity with Temperature and Pressure.—The engineer must frequently estimate the viscosity of an oil at another temperature than 100 or 210°F. This may be done by means of Fig. 48 (page 125), but great accuracy is possible by use of the Herschel viscosity diagram (Fig. 47). In order to use this chart it is necessary to know the viscosity at one temperature and the base of the oil. The kinematic viscosity and the viscosity in centipoises can be obtained by the use of Eq. (2), page 43.

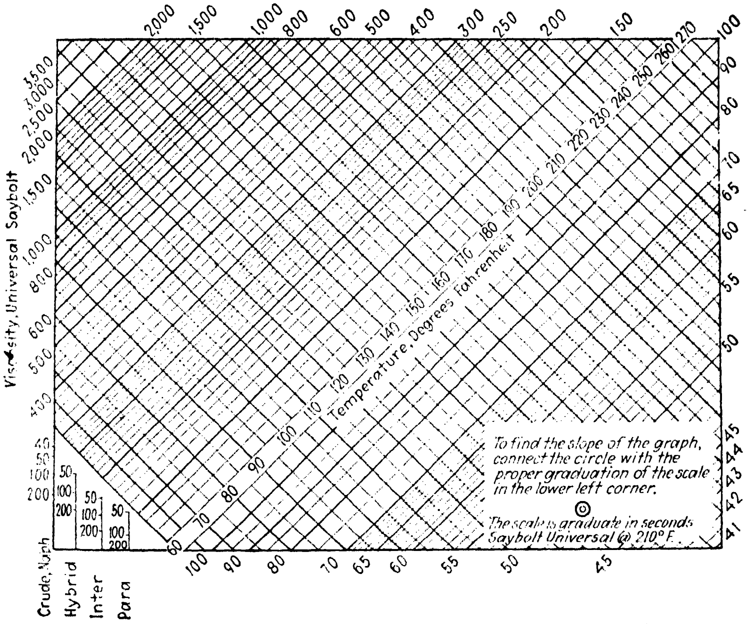

Fig. 47.—Herschel viscosity diagram. (*Courtesy of The American Instrument Company.*)

The A.S.T.M. supplies four large charts[13] that are more accurate than Fig. 47 and can be used for kinematic as well as Saybolt viscosity units.

Example 18. Viscosity at Different Temperatures.—A paraffin-base oil has a viscosity of 90 at 210°F. What is its viscosity at 160°F.?

In using Fig. 47 a line must be drawn across the diagram. The slope of this line is determined by connecting the circle in the lower right corner with a point on one of the scales in the lower left corner. In this problem the 90 point on the paraffin scale should be used.

A line is drawn through the point for 90 viscosity at 210°F., having a slope as indicated above. Follow this line until it crosses the 160°F. line. This point is located among the viscosity lines and is found to be 195 Saybolt seconds at 160°F.

If the specific gravity of the oil is 0.865 at 160°F., the viscosity in centipoises can be obtained by Eq. (2), page 43.

$$\frac{z}{s} = 0.219t - \frac{149.7}{t}$$

$$z = 0.865\left(0.219 \times 195 - \frac{149.7}{195}\right) = 36.2$$

Recently it has become common practice to measure the rate at which viscosity changes with temperature by means of the Viscosity Index. This relation is discussed on page 69 (see also Figs. 16, 17, Chap. VII).

The relation between viscosity in centipoises and temperature given in Fig. 48 is probably not so accurate as other methods

TABLE 10.—OILS USED IN PLOTTING FIG. 48

Curve No.	Material	A.P.I.	Viscosity at		Viscosity index
			100	210	
1	Natural gasoline	76.5			
2	Gasoline	57.0			
3	Kerosene	42.0			
4	Distillate	35.0	35		
5	Gas oil	30.0	50		
6*A*	Lube	32.0	60	40	100
6*B*	Lube	21.0	130	40	0
7*A*	Lube	29.0	255	50	100
7*B*	Lube	19.0	440	50	0
8*A*	Lube	28.0	780	80	100
8*B*	Lube	16.0	1,640	80	0
9*A*	Lube	26.0	1,730	125	100
9*B*	Lube	14.5	4,400	125	0
10	Lube	20.0	.....	200	70
11	Residuum	19.8	.....	300	70
12	Asphalt	....	(50 penetration)		

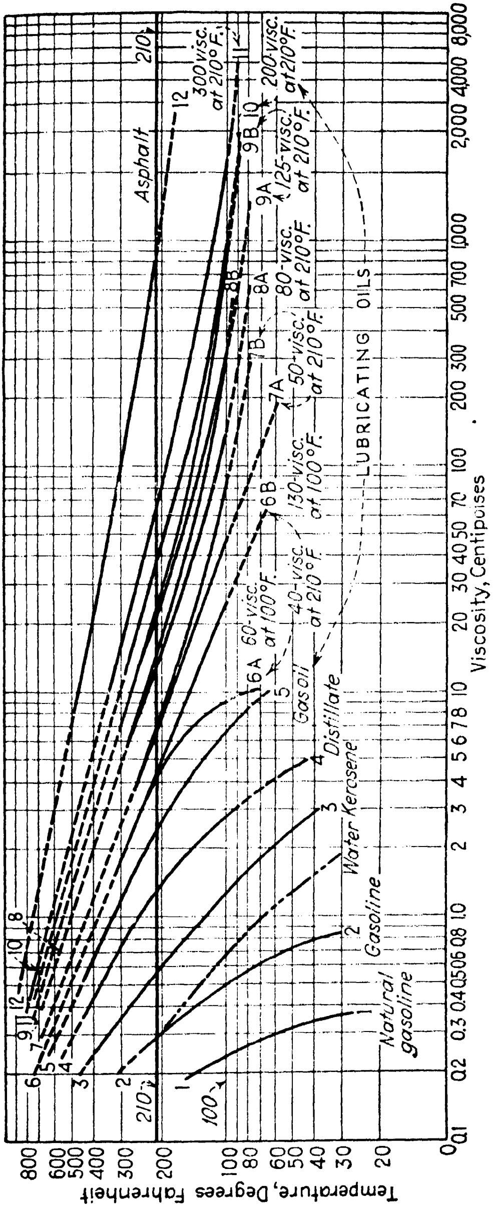

FIG. 48. Relation of viscosity and temperature of petroleum oils.

that have been presented, but the chart is convenient to use and is sufficiently accurate for many design purposes. For further convenience, Table 10 shows the properties of the oils used in computing Fig. 48.

The effect of pressure upon the viscosity of liquids is not great at normal operating pressures, but at a pressure of 1,000 lb. per square inch and upward its effect is astoundingly great.[14] As a general indication of the effect of pressure, the viscosity is increased about 15 per cent at 1,000 lb., three- to eightfold at 10,000 lb., and upon exceeding 55,000 lb. per square inch most oils begin to solidify.

Viscosity of Gases.—Data on the viscosities of gaseous hydrocarbons and petroleum vapors are not extensive, but what data are available are found to agree well with Fig. 49.[15] For mixtures of gases, the pseudo critical-point of the mixture may be used with fair accuracy.

In general, conditions at which the materials will be liquids are on the upper part of the chart, *i.e.*, above the reduced temperature line marked 1.0, whereas the viscosities of gases are near the bottom of the chart and below a reduced temperature of 1.0. The viscosity of liquids decreases with temperature (moving downward toward higher values of reduced temperature) and the viscosity of low pressure gases increases with temperature. Both of these effects are apparent on the chart but also note that at high pressures and high temperatures the viscosity of gases (or fluids) decreases with temperature in the same manner as true liquids.

A somewhat more accurate correlation may be obtained by utilizing the viscosity at the high pressure over the viscosity at atmospheric pressure, rather than plain viscosity,[16] but the small amount of data that are now available do not appear to justify this added complication.

The viscosity of natural gas has been studied by Berwald and Johnson.[17] Except for the gases that contain abnormal amounts of nitrogen, oxygen, or carbon dioxide, the information of these authors indicates that all natural gases have about the same viscosity—and the viscosity may be taken as 0.0105 at room temperature for most purposes.

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[14] Dow, Fenske, and Morgan, Effect of Pressure on Viscosity of Oils and Chlorinated Diphenyls, *Ind. Eng. Chem.* **29**, 1078 (1937).

[15] Nelson, W. L., Viscosity of Gases Handled in Distillate Plants, *Oil Gas J.*, July 13, 1939, p. 50.

[16] Comings and Egly, Viscosity of Gases and Vapors at High Pressures, *Ind. Eng. Chem.*, **32**, 714 (1940).

[17] Viscosity of Natural Gas, *U.S. Bur. Mines, Tech. Paper* 555, 1933.

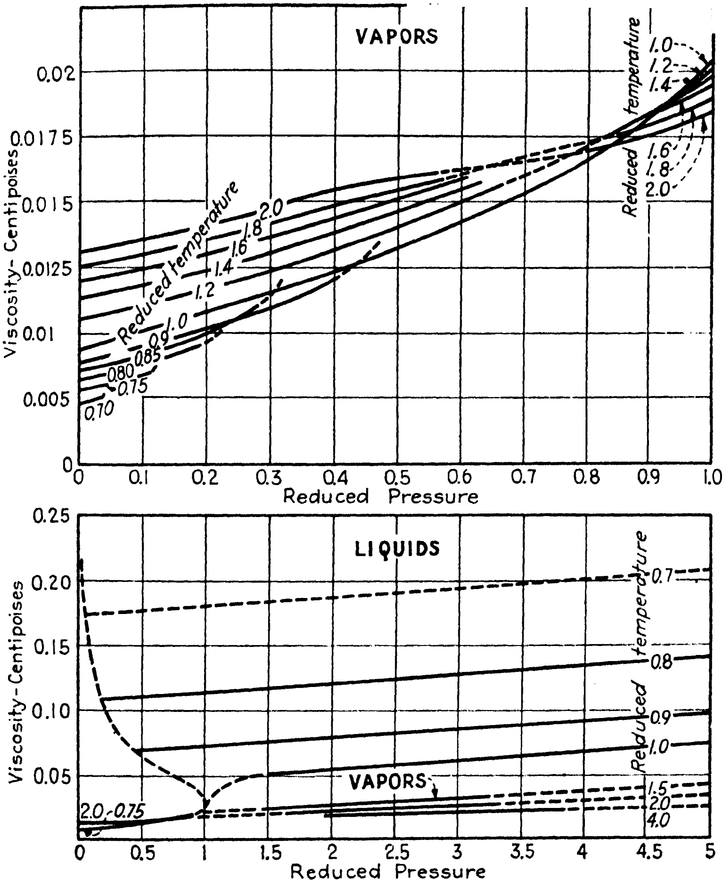

FIG. 49.—Viscosity of hydrocarbon liquids and vapors.

Heat of Combustion.—The heat of combustion of petroleum oils increases with A.P.I. gravity (or hydrogen content) as indicated in Fig. 50.[18] The figure is accurate within about 1 per cent if the percentage of water, ash, and sulfur is accounted for.

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[18] CRAGOE, C. S., Thermal Properties of Petroleum Products, *Nat. Bur. Standards Misc. Pub.* 97, 1929.

Cracked fuel oils have a higher heating value than straight-run products.[19] Tables 25 and 26 on pages 176 and 177 give analyses and heating values of various refinery fuels.

Vapor-pressures of Oil Fractions.—A study of mixtures requires a revision of our conception of vapor-pressure. Every material, by virtue of the movement of molecules within it, exerts a tendency to vaporize, even though it is far below its boiling-point. In the case of a single compound the tendency to vaporize or to project molecules of itself into the surroundings becomes greater and greater as the temperature is raised, until it is equal to the pressure of the system, and the material is said to boil. At temperatures above the boiling-point the vapor-pressure is greater than atmospheric pressure, and a convenient method of measuring such vapor-pressures is to apply enough pressure to suppress boiling.

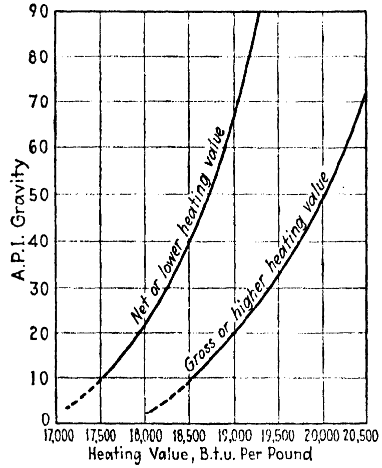

FIG. 50.—Relation of heating value and A.P.I. gravity. (*U.S. Bureau of Standards.*)

A mixture tends to behave differently because it does not boil at one temperature. The vapor-pressure of a mixture is usually defined as the pressure exerted by the material when no vaporization occurs. If vaporization occurs, the composition of the material is no longer the same. The vapor-pressure of a mixture is a summation of the vapor-pressures of each of its components (Raoult's law, page 229), and hence the vapor-pressure should be a function of the slope of the distillation curve.

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[19] FARAGHER, MORRELL, and ESSEX, *Ind. Eng. Chem.*, **21**, 933 (1929).

An excellent correlation of the vapor-pressures of gasoline is presented by Meyer,[20] and Bridgeman[21] presents the dew-points of gasolines as a function of the A.S.T.M. distillation curve.

Boiling-point Corrections.—The conversion of boiling-points from one pressure to another is of prime importance to the designer. A distillation conducted at a constant pressure is equivalent to changing the temperature and composition of the material simultaneously so that the vapor-pressure always equals the pressure at which the distillation is being conducted. If several distillations of the same material are conducted at different pressures and the same degree of fractionation is maintained throughout all of the distillations, we have a means of plotting vapor-pressure curves. If any percentage distilled is selected, the residue in the flask exerts a vapor-pressure that is equal to the pressure in the flask. Thus boiling-point corrections involve vapor-pressure and may be correlated by the same methods as those used in correlating vapor-pressures. However, the correlation of boiling-point corrections is involved because (1) the slope or distillation range of commercial products varies, (2) the

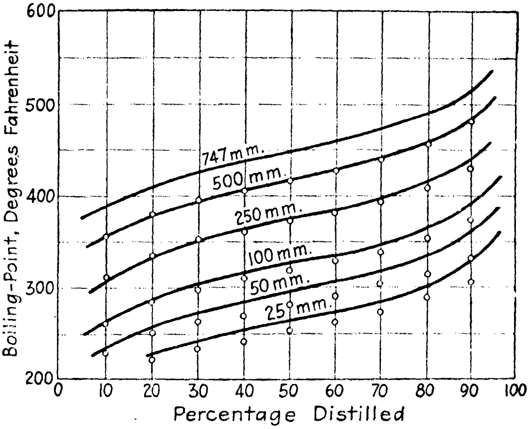

FIG. 51.—Vacuum distillations of kerosene.

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[20] The Vapor Pressure Curves of Petroleum Spirits, *J. Inst. Petroleum Tech.*, **17**, 42 (1931).

[21] Dew Points of Air-gasoline Mixtures from Distillation Curves, *Ind. Eng. Chem.*, **20**, 821 (1928).

manner of vapor formation may differ, and (3) the chemical composition of oils differs. Figure 51 presents a series of distillations of Mid-Continent kerosene. The circle points were computed by using the vapor-pressure chart for the paraffin hydrocarbons (Fig. 52).

Inherently the true-boiling-point curve should be most easily correlated because it consists of the boiling-points of nearly pure compounds as they distill one by one. The equilibrium-flash curve illustrates the other extreme type of distillation, and corrections of this curve from one pressure to another should not be exactly the same as the correction for fractionating distillations. Nevertheless, a large difference does not seem to exist between these two extremes of boiling-point corrections, nor does the slope of the distillation curve seem to alter the vapor-pressure or boiling-point corrections to a great extent.

Piromoov and Beiswenger[22] find that the slopes of flash-vaporization curves are practically independent of pressure, so that the correction of the boiling-point or flash-vaporization point is a constant number of degrees throughout the entire curve. They suggest that the correction should be determined by correcting the intersection point between the true-boiling-point curve and the flash-vaporization curve by the vapor-pressure data of the paraffin hydrocarbons. The intersection point is used because the true-boiling point curve and the flash-vaporiza-

TABLE 11.—REDUCTION OF BOILING-POINT BY VACUUM, DEGREES FAHRENHEIT

Pressure, mm.	For oils that boil at the following atmospheric boiling-points:						
	300	400	500	600	700	800	900
760	0	0	0	0	0	0	0
500	25	29	32				
200	74	82	90	96	101	107	
100	106	117	130	137	143	153	161
50	137	151	167	179	186	196	208
20	...	190	215	227	238	254	270
10	...	...	252	267	280	298	316
5	...	...	...	305	323	342	364

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[22] Equilibrium Vaporization of Oils and the Carrying Effects of Light Ends, *A.P.I. Bull.* 10, No. 2, Sec. II, p. 52, 1929.

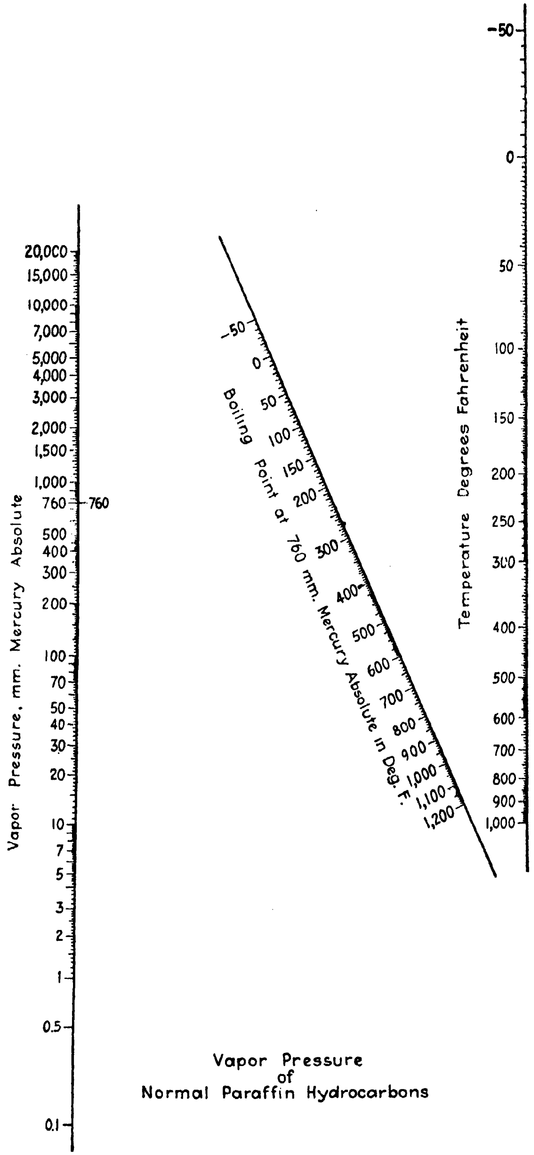

FIG. 52.—Vapor-pressure and boiling-point corrections for the normal paraffin hydrocarbons.

tion curve intersect at approximately the same percentage point regardless of pressure.

A study of several distillations similar to Fig. 51,[23] as well as some scattered data on boiling-point corrections in the technical literature, has failed to reveal all the factors that are involved in correcting boiling-ranges from one pressure to another. However, Table 11 shows the approximate change in boiling-point that is caused by distillation at a reduced pressure, as obtained from distillations[23] such as the one shown in Fig. 51.

Obviously the correlation of vapor-pressures and boiling-point corrections for commercial mixtures is still in a formative stage. Apparently the vapor-pressures of the normal paraffin hydrocarbons are our most dependable data, but they are not exact when applied to oils. However, if the laboratory data are converted from vacuum conditions to atmospheric pressure by means of Fig. 52 and the same chart is used during design calculations in determining boiling-points under vacuum, errors are eliminated to a large extent by the two operations. Figure 52 will be used throughout this book for boiling-point corrections.

Example 19. Correction of Boiling-point to Another Pressure.—An oil has a boiling point of 500°F. at atmospheric pressure. At what temperature will it boil if the pressure is 50 mm.? (Refer to Fig. 52.)

A line is drawn across the chart connecting 50 on the left scale with 500 on the center scale. The temperature may be noted on the right scale.

B.P. at 50 mm. = 329°F.

Discussion.—The rapid rate at which data regarding petroleum mixtures are being accumulated should always be borne in mind. Much of the data in this chapter will soon need to be revised. Much of the data are still in a poor state of correlation. Nevertheless, the use of the data such as they are is necessary, and judgment must be used accordingly. The oil industry should cooperate in determining the true properties of petroleum hydrocarbons and oil mixtures. Such a program would doubtless result in a new and astounding petroleum chemical industry.

There is hardly an end to the properties of petroleum oil that might be discussed in this chapter, but many of them can be better presented as they are needed in definite problems.

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[23] Samples of Mid-Continent crude oil, gasoline, kerosene, gas oil, wax distillate, pressed distillate, lubricating oil, Gulf Coast crude oil, and cracked gas oil have been examined.

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CHAPTER IX

REFINERY PRODUCTS

The underlying purpose of all refinery processing is the production of marketable products. Because of this fundamental purpose, a study of the uses and specifications of finished refinery products provides a broad understanding of the necessity for the various refining operations.

The large number of compounds constituting petroleum permits a single product to exhibit a wide range of physical properties. The boiling-range of crude petroleum ranges evenly from less than −100 to perhaps 1300°F., and the specific gravity from 0.6 for the lightest fractions to more than 1 for the highest boiling portion. During processing, the crude oil is separated into products, each product embracing a certain range of the foregoing physical properties. Obviously many different products can be made, depending upon the uses for the product and upon the limiting market specifications. Petroleum oil specifications usually allow a relatively wide range of physical properties. As an example, consider gasoline. Gasoline is not a distinct, uniform product. Depending upon the sales region and upon its use, gasoline may have an end-point between 320 and 437°F. and may vary in gravity between 50 and 70 A.P.I. Thus the amount of gasoline that may be produced from crude oil will vary widely not only because of differences in crude oils but also because many different gasolines may be produced. The same condition exists regarding many other refinery products.

In general, finished refinery products may be grouped as follows:

1. *Light oils*—gasoline, naphtha, solvents, and burning-oils.
2. *Distillates*—fuel oil, diesel fuel, tractor fuel, and gas oil.
3. *Lubricating oils*—motor oils, engine oils, machine oils, etc.
4. *Greases and waxes*—cup grease, salve bases, and paraffin wax.
5. *Residues*—fuel oil, coke, asphalt, carbon black, etc.
6. *Specialties*—medicinal products, insecticides, alcohols, etc.

G. A. Beiswenger[1] presents a vital discussion of the specifications of various products, the choice among crude oils from the standpoint of specifications, and the economy of evaluating crude oils.

Light Oils.—Gasoline is perhaps the most important petroleum product. United States government agencies[2] specify six motor fuels. U.S. Motor Fuel is a somewhat poor grade for automotive engines; Fuel V is a special grade for ambulances, fire engines, emergency vehicles, etc., and the four aviation gasolines grade upward in octane number, being used for break-in, training, and

TABLE 12.—GASOLINE SPECIFICATIONS

Name or grade	Maximum distillation range, °F.				Gum, mg. per 100 ml.	Maximum sulfur, per cent	Vapor-pressure, (Reid)	Octane* number minimum
	10 per cent	50 per cent	90 per cent	E.P.				
Government:								
1. Aviation, fighting	158–167	212	275	......	6	0.05	7	100
2. Aviation	158–167	230	320	......	6	0.05	7	65–91
3. U.S. motor	149–167	284	392	......	..	0.1	12	
4. Fuel V	149	257	356	......	..	0.1	10	65–75
A.S.T.M., D439 37T:†								
5. Type A-regular	140–158	284	392	......	7	...	9.5–13.5	67–75
6. Type B-volatile	140–158	257	356	......	7	...	9.5–13.5	67–75
7. Type C-non-volatile	167	284	392	......	7	..	9.5–13.5	45
Aviation fuels:								
8. Average airlines (1938)	158–167	191–221	231–347	......	6	0.1	6.5–7.5	73–95
9. Blending naphtha‡	120–140	175–205	235–250	265–295	..	...	7.0	70–76
Average fuels:§	Average distillation range, deg. F.						(Average)	(Average)
10. 1928 regular	146	267	379	426	..	...	....	56
11. 1931 regular	148	255	373	411	.	..	6.4	60
12. 1934 regular	135	242	354	403	.	...	9.5	69
13. 1937 regular	125	240	358	401	..	...	10.3	70
14. 1939 competitive	142	245	357	405	..	...	8.0	62
15. 1939 regular	127	225	352	396	..	..	10.6	73
16. 1939 premium	127	220	347	393	..	...	9.9	80

* Maximum tetraethyl lead allowed is often specified.

† Petroleum Products and Lubricants, A.S.T.M., 260 South Broad Street, Philadelphia, Pa.

‡ Straight-run naphtha suitable for blending with isooctane, isopentane, etc., for 100 octane number fuel.

§ ZIEGENHAIN, W. T., A yearly review, *Oil Gas J.*, June 8, 1939. Really winter fuels taken during late winter.

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[1] Factors Affecting the Refiner's Choice of Crudes, "Petroleum Technology in 1939," A.I.M.M.E., New York, 1939.

[2] U.S. Motor, VV-G-101a, Motor Fuel V, VV-M-571*a*, and Aviation fuels, AN-VV-F 756, 761, 776, and 781, Superintendent of Documents, Washington, D.C.

fighting purposes. Some of the specifications of typical motor fuels are given in Table 12.

The A.S.T.M. specifications are perhaps the most comprehensive. In addition to the three types of gasolines specified in Table 12, the types are further divided according to volatility to care for seasonal changes and according to octane number to care for compression ratio, as indicated in the following tabulations:

	10 per cent point	Vapor-pressure
Cold or winter (W)	140	13.5
Medium (F)	149	11.5
Warm or summer (S)	158	9.5

	Octane Number
Premium price	75
Regular price	67
Low price	45

All parts of the United States have been classified as W, F, or S areas, as used above, with regard to climatic conditions during each month of the year.

The most significant properties of motor fuels may be summarized as follows:

1. Antiknock quality.
2. Volatility.
3. Vapor-pressure.
4. Amount of sulfur and gum.

Other properties such as color, gravity, initial boiling-point, and end-point have been found to be of secondary importance. *Volatility* measures the ease with which a cold engine can be started and also the rate at which the engine will respond to the use of the throttle during acceleration. The curvature of the A.S.T.M. distillation curve is considered as the best indication of the volatility. The 10, 35, 65, and 90 per cent points are particularly significant.[3] The 10 per cent point must be low enough to allow sufficient vaporization to start the cold engine with a minimum number of revolutions of the motor and at the same time must not be so low as to promote vaporization in the gasoline feed system. The 35 and 65 per cent points are related to the performance of the car after the motor is started; and the 90 per cent point must not be too high, or crankcase dilution and a loss of power will result. The *vapor-pressure* is a check on the possibility of vapor-lock in the feed system. The percentage of propane in the fuel is important in governing the tendency for vapor-lock. One per cent propane increases the vapor-pressure of most fuels by about 2 lb.

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[3] Brown, G. G., The Volatility of Motor Fuels, *Eng. Research Bull.* 14, University of Michigan, 1930, p. 7.

With the advent of high-compression motors, the tendency of a fuel to *spark-knock* or *detonate* violently has attracted much attention. Knocking is thought to be due to autoignition of part of the charge in front of the flame. Mild knocking has little effect on the performance of the engine, but severe knock may result in loss of power and damage to pistons or bearings. Certain substances such as lead tetraethyl[4] and iron carbonyl[5] tend to prevent knocking. All hydrocarbons have different antiknock properties, and certain of these, such as benzol[6] and those in cracked gasoline, are useful in suppressing knocking. Standard ethyl gasoline has an octane number of 78 (1940), and the Q grade of Ethyl gasoline must not have an octane number exceeding 70 by the motor method. Octane number is greatly affected by altitude.[7] The octane number may be about three units lower for each 1,000 ft. of elevation at elevations near sea level (growing to 7.5 per 1,000 ft. at 12,000-ft. elevation). Thus, if an octane number of 67.5 is necessary at sea level, an octane number of 50 is satisfactory at 6,000-ft. elevation, and at 12,000-ft. elevation a number of even 20 is satisfactory.

Cracked gasoline often contains *gumlike materials* that are deposited on the glasses of filling-station pumps and on the walls of the intake manifold and valves[8] of an engine. Gasolines containing 10 mg. of preformed gum per 100 ml. give little or no trouble; 20 or 25 mg. frequently causes sticking of the valves; and over 50 mg. usually results in sticking valves and carbon deposition.[9] It appears that carbon deposits are related to gum content if the engine manifold is unheated but no such relation exists if the manifold is heated.[10] The rate of gum formation during storage has been related to the time required to produce 10 mg. of gum in a laboratory accelerated oxidation test,[11] and hence it is now possible to foretell the length of time that a gasoline can be stored. Chemical inhibitors which delay the formation of gum are widely used.

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[4] Midgley, Thomas, Jr., Tetraethyl Lead Poison Hazard, *Ind. Eng. Chem.*, **17**, 827 (1925).

[5] "Motalin," a blending compound of the I. G. Farbenindustrie A.G.

[6] Campbell, Lovell, and Boyd, Standard Fuel for Anti-knock Quality, *Oil Gas J.*, Jan. 23, 1930, p. 42.

[7] MacCoull, Hollister, and Crone, Effect of Altitude on Anti-knock . . . , *Ref. Nat. Gaso. Mfr.*, November, 1937, p. 534.

[8] Voorhees and Eisinger, The Importance and Significance of Gum in Gasoline, *Oil Gas J.*, Dec. 20, 1928, p. 152.

The amount of *sulfur* that can be safely allowed in gasoline has been a much-discussed question. Quantities as high as 0.2 per cent usually will not cause serious corrosion difficulties, and gasolines containing 0.25 per cent sulfur are being marketed in a few parts of the United States. Nevertheless, owing to disastrous results with certain high-sulfur oils, the quantity of sulfur is usually limited to 0.1 per cent.

The *color* of gasoline indicates little about its quality, although it is an indication of the thoroughness of the refining operation and of the tendency to produce gum. The highly desirable antiknock compounds are partly removed by treating, and hence the specification of color has become less and less important. Most refiners resort to the use of oil-soluble dyes to mask the color of the natural product. Dyes ranging in color from yellow to dark purple are available.[12] These dyes also serve (1) to identify a gasoline and thus promote confidence in its advertised quality, (2) to preserve the antiknock properties that would be partly lost during chemical treatment, and (3) to reduce the cost of refining.

The demand for volatile and antiknock fuels has promoted the development of the natural-gasoline industry, cracking processes, and polymerization processes. Our motor fuels consist of natural gasoline for volatility, cracked gasoline or antiknock substances for allaying the tendency to knock, straight-run gasoline which usually constitutes the main bulk of the product, and sometimes coloring agents or gum inhibitors.

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[9] TRUSTY, A. W., Gum in Gasoline . . . , *Ref. Nat. Gaso. Mfr.*, February, 1935, p. 47.

[10] MARLEY, MARTIN, and GRUSE, . . . Moderate Gum Content in Gaso. Not Harmful, *Oil Gas J.*, Nov. 10, 1932, p. 12.

[11] YABROFF and WALTERS, Gum Formation in Cracked Gasolines, *Ind. Eng. Chem.*, **32,** 83 (1940).

[12] EGLOFF *et al.*, Dye Saves Dollars in Treating Gasoline, *Oil Gas J.*, Mar. 5, 1931, p. 133.

The term *naphtha* is used to refer to any light oil product having properties intermediate between gasoline and kerosene. The various solvents, in general called *industrial naphthas,* are special products sold in small quantities and at special prices. In Table 13 are listed some common naphthas and their uses. So many different properties are required that each solvent must receive individual attention. Among the special requirements may be white color; low unsaturated and aromatic content for stability; high aromatic content for solution of lacquers or synthetic resins; or low boiling for rapid volatilization. In general, however, naphthas should be free from acidity, noncorrosive by the copper-strip test, free from gums or suspended matter, sweet smelling so that a petroleum odor is not imparted to the manufactured products, and well fractionated to eliminate as much of the fire hazard as possible. Much of the data given in Table 13 were taken from "The Science of Petroleum."[13]

Recently the art of distillation and fractionation has been developed to such a degree that pure compounds or nearly pure compounds can be prepared from petroleum. Among these compounds are propane, butane, pentane, and the corresponding *iso* compounds. Several of these have already been offered on the market, and doubtless during the next few years they will find a widespread use as commercial solvents. Commercial butane is sold for gas manufacture, and nearly pure propane is sold as a bottled gas for cooking purposes.

The mineral-oil solvents should not be considered as substitutes for other solvents that are now used, because mineral solvents possess properties that are unique and useful, and for many purposes they can be selected because of their own merits.

The *burning-oils* represented by kerosene, long-time burning-oil, lighthouse kerosene, and 300°F. mineral seal oil, as their names imply, are used as fuels in household, marine, passenger-coach, and railroad illuminating lamps. Kerosene is the common household, marine, and government burning-oil. The 300° mineral seal oil is a high-grade oil having a Cleveland open-cup

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[13] HARRAP, F. N., Industrial Petroleum Solvents and White Spirits, Vol. III, p. 2462 Oxford University Press, New York, 1938.

TABLE 13.—SPECIAL SOLVENTS AND NAPHTHAS

Name and use	A.P.I.	Distillation range, deg. F.					Aromatic hydrocarbons, per cent by weight	Kauri butanol number	Dilution ratio	
		I.B.P.	10 per cent	50 per cent	90 per cent	E.P.			Butyl acetate	Ethyl acetate
1. Volatile—rubber cement solvent....	78	82	111	147	191	222				
2. Rubber goods solvent.............	69.5	113	144	176	203	239	7	32	1.22	
3. Seed and perfume extraction.......	68	158	...	169	...	194	2	32	1.22	1.15
4. Paint remover, dry cleaning, tire manufacture solvent..............	55	230	243	253	279	320	12	37	1.25	
5. White spirits—dry cleaning, paint and varnish thinners, shoe polishes, floor and furniture polishes, and metal polish pastes..............	42–54	307	316	331	356	383	16–45	32–46	(Tag flash-point 48°F.)	
6. Stoddard solvent and mineral spirits—dry cleaning and paint thinners	49	300	318	350	375	410	.....	.....	(Tag flash-point 100°F.)	
7. Cellulose lacquer diluent, printer's ink..........................	53	167	...	176	...	203	25	49	1.55	
8. Leather degreasing, cellulose lacquer diluent, printer's ink, and tire manufacture....................	45–47	210–240	...	225–260	...	248–320	44	54	1.62	1.55
9. Paint thinner (synthetic resins).....	32.3	365	380	385	394	410	60	56	1.65	

flash-point of not less than 250°F. Signal oil for railroad lamps is compounded from 300° mineral seal oil and lard or sperm oil. Long-time burning-oil is the finest grade, and in the burning test 650 cc. of oil must not be consumed in less than 120 hr.

The value of kerosene is directly dependent upon its behavior in the burning or lamp test. An unsatisfactory burning test is terminated by smoking, by a white cloud in the chimney, or by a "toadstool" formation on the wick. Smoking is due primarily to aromatic hydrocarbons; a white cloud is probably produced by disulfides (over 0.01 per cent); and toadstools are thought to be related to both aromatics and disulfides. The Saybolt thermoviscosity is also a good indication of the behavior of the oil in a lamp. The viscosity usually ranges between 325 and 450. However, an oil may have a proper viscosity and yet fail to burn satisfactorily. Kerosenes may have a gravity of 38 to 48 A.P.I. and a flash-point (Tag) of 120 to 180°F. The initial boiling-point is usually about 370°F., and the end-point about 500°F., although the government allows an end-point of 620°F. Although the gravity is not important, many refiners strive to produce a 41.5 to 43 A.P.I. kerosene, and hence most of the kerosene on the market has this gravity. A small amount of light material (naphtha) is necessary in order to produce a high-quality burning-oil. For this reason a little heavy gasoline must always be present in the kerosene, and hence the boiling-ranges of kerosene and gasoline (or naphtha) overlap to some

TABLE 14.—KEROSENE AND RELATED DISTILLATES

Name of product	Gravity, A.P.I.	Flash point (Tag), deg. F. min.	Color	Sulfur, per cent max.	Distillation, deg. F.		Recovery, per cent	Burning test, hr.
					I.B.P.	E.P. max.		
41–43 W.W. (domestic)	42–44	130	30	0.05	365	485	98	24
Standard White	38 min.	130	..	0.10	375	500	98	24
44–46 W.W.	44–46	130	30	0.025	365	485	98	24 (and 21 day)
Long-time burning-oil and 325 W.W.	46–48	125	30	0.05	320	475	98	24 (and 14 day)
300 oil	36–39	260	..	.....	510	660	..	(for 300 oil)
Tracter fuel	38–41	80–115	..	0.10	300	465	..	(Octane 43–55)
Stove oil	43	......	25	0.07	...	530		

extent. If the gasoline (or naphtha) and kerosene are too well fractionated, the flash-point and initial boiling-point of the kerosene will be so high that it will not burn properly. This overlapping of cuts must always be considered when the gasoline and kerosene are evaluated from a crude-oil distillation curve.

The color instability of some kerosene has at times been a mysterious difficulty. Several inhibitors and tests for color instability have been developed.[14] The properties of a few kerosenes and related distillate products are given in Table 14.

Distillates.—Among the so-called distillates are included domestic fuel oils (stove distillates), diesel fuel oil, tractor oil, spray oils, insecticides, smudge oil, straw oil, absorption oils, industrial (distilled) fuel oils, and gas oil. Table 15 presents the properties of some of these distillates. This table indicates that the properties of distillates are not closely specified. Distillates are cheap, and hence they are usually given little attention in the refinery. Excess stocks of gas oil, the distillates, and even the heavy portion of gasoline are disposed of by cracking or reforming into cracked gasoline. Often the refiner blends his

TABLE 15.—DISTILLATE OILS

Grade or name	Flash-point, deg. F.	A.P.I.	Pour-point, max., deg. F.	Distillation range, deg. F.			Vis-cosity at 100°F	Water and sedi-ment, per cent	Others
				I.B.P.	Max. 10%	Max.			
1. Volatile domestic	100-165	42	0	.	410	560	..	Trace	0.05 carbon residue*
2. Medium domestic	110-190	38	10	...	440	600†	..	0.05	0.25 carbon residue*
3. Heavy domestic	110-230	34	20	...	...	675†	45	0.10	0.15 carbon residue
4. Quality diesel	170	37	0	392	440	645	35	....	57 Diesel Index
5. Medium diesel	170	33	0	430	470	700	38	....	48 Diesel Index
6. Tractor fuel	110	39	..	250	347	500	..	....	56 octane number
7. Gas oil (gas enrichment)	195	33	..	302	460	700+	35		
8. Industrial fuel	210	30	35	440	475	800+	70		
9. Absorption oil	......	45	..	344	386	505	..	....	Demulsibility 9 min.
10. Absorption oil	......	37	..	482	518	630	39	....	217 molecular weight

* On 10 per cent residuum.

† 90 per cent point.

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[14] HILLMAN, McHATTON, and MOERBEEK, *Proc. World Petroleum Cong.*, **2**, 704, 708, 713, and 721 (1933); and RATHER and BEARD, *Ref. Nat. Gaso. Mfr.*, **15**, 217 (1936).

distillates, along with other similar products such as pressure distillate "butts," with heavy tar to reduce the viscosity of the tar so that it can be marketed as a fuel oil.

The Diesel Index[15] defined as the aniline point (degrees Fahrenheit) times the A.P.I. gravity, divided by 100, is assuming importance as a criterion of the ignition qualities of diesel fuels. A high index indicates good ignition quality, and the range of Diesel Index for common fuels is 30 to 80.

All of the distilled industrial fuels come from this group. The only properties that require much attention are the flash-point and sulfur content. Originally, gas oil was widely used for enriching artificial gas, but today most of it is used as a fuel or cracked into gasoline. Distillates are also being used as insecticides in swamps and for spraying trees, although residual fuel oils are more generally used.

TABLE 16.—AUTOMOTIVE LUBRICATING OILS

S.A.E. No.	Saybolt Universal visc. at 130°F.	Saybolt Universal visc. at 210°F.	Flash-point, deg. F.	Pour-point, deg. F.	Color A.S.T.M.	Carbon residue, per cent	Sligh oxidation No.	Neutralization No.
20	120 or 185	47 55	400	0	5	0.10	20	0.1
30	185 or 255	55 63	410	0	6	0.15	20	0.1
40	255 or 367	63 75	425	5	7	0.25	20	0.1
50	367 or 654	75 105	445	10	7	0.40	20	0.1
60	654 or 855	105 125	475	15	8	0.70	20	0.1
70	855 or 1114	125 150	510	15	8	1.00	20	0.1

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[15] BECKER and FISCHER, A Suggested Index of Diesel Fuel Performance, *J. Soc. Automotive Eng.*, October, 1934, p. 376.

Lubricating Oils.—The wide usefulness of mineral lubricating oils does not permit a discussion of all of them. Among these oils are motor oils; tractor oils; motorcycle oils; aero oils; engine and machine oils; locomotive and car oils; aircraft and machine-gun oils; gun and ice-machine oils; recoil oils; gear, chain and wire-rope oils; penetrating oils; transmission oils; putty oils; wool oils; spindle oils; thread-cutting oils; tempering and quenching oils; insulating oils; stainless oils; harness oils; floor oils; furniture and automobile polish; cutting oils; buffer oils; denaturing oils; medicinal mineral oils (white); and technical white oils. Technical white oil is particularly interesting because it is used to lubricate the machinery in food-manufacturing plants, such as bakeries and candy factories, and for lubrication in certain textile work.

The properties of oils that are desirable for automotive internal-combustion engines are summarized in Table 16, which is taken primarily from United States Federal Specification[16] VV-0-496.

The S.A.E. have assisted greatly in classifying oils by introducing the following number system for lubricating oils. For winter service the S.A.E. 10 and 20 grades may be replaced by 10 W and 20 W oils, which have viscosities at 0°F. of 5,000 to 10,000 and 10,000 to 40,000 sec. respectively.

S.A.E. No.	Saybolt Universal viscosity, at		
	100°F.	130°F.	210°F.
10	....	90–120	
20	231– 384	120–185	50– 60
30	384– 550	185–255	60– 69
40	550– 652	255–293	69– 80
50	652–1244	293–397	80–105
60	....	....	105–125
70	....	....	125–150

The important common tests for an oil are (1) flash- and fire-points, (2) viscosity and viscosity-index, (3) color, (4) pour-point, (5) corrosion, (6) emulsibility or demulsibility, (7) carbon residue, and (8) precipitation.

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[16] Lubricating Oil, Class *D*, Superintendent of Documents, Washington, D. C.

The *flash-* and *fire-*points indicate the amount of light material (gas oil) in the lubricating oil. Naphthene-base oils have lower flash-points than other oils of the same boiling-range. Low-flash oils tend to be distilled into the exhaust of an automotive engine. However, the effect of the flash-point on lubricating ability should not be overemphasized because a low-flash oil always exists in the engine after a few miles of operation because of crankcase dilution. The flash-point is widely used as an indication of the degree of fractionation that the oil has undergone and the base from which it was derived. The Standard Oil Company of Indiana markets a motor oil under the name "Isovis." This oil is diluted with a lighter oil at the refinery so that it already has the composition of an oil that has been diluted by crank case dilution.

Much importance has been attached to *Viscosity Index*[17] because it measures the suitability of an oil to lubricate properly at the elevated temperature of the engine and at the same time not to be too viscous for operation while the engine is cold. Engines start satisfactorily if the viscosity does not exceed about 40,000 sec.[18] Saybolt Universal, and hence the lowest temperatures at which the various oils should be used, provided the pour-point is low, are somewhat as follows:[19]

Viscosity at 210°F.	Lowest temperature for easy starting, deg. F.	
	Zero viscosity index	100 viscosity index
55 (S.A.E. 20)	27	−10
60	33	− 2
70	41	9
80	46	15
90 (S.A.E. 50)	50	20

The major usefulness of determining the *color* is to indicate the nature of the refining operation. Nevertheless, some companies have so improved the color that the costs of refining have been needlessly increased.[20] The *pour-point* indicates the tendency of an oil to congeal at low temperatures and thus fail to lubricate. Most oils are now dewaxed to pour-points lower than 0°F. Low pour-point oils are uniquely valuable for certain purposes such as for airplane oils, aircraft machine-gun oil, recoil oil, ice-machine oil, and motor oils in cold climates. *Emulsibility* or *demulsibility* is particularly important for oils that must be used in the presence of water or steam and for lubricating high-speed machines such as turbines. The *carbon residue* supposedly measures the tendency of an oil to deposit carbon in the internal-combustion engine. Wilson and Barnard[21] conclude that the carbon residue indicates the amount of carbon formation that will occur but

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[17] See Figs. 16 and 17 for viscosity temperature relationships.

[18] Otto, Miller, Blackwood, and Davis, Improved Motor Oils, *Ref. Nat. Gaso. Mfr.*, November, 1934, p. 411.

[19] Nelson, W. L., Significance of Viscosity . . . , *Oil Gas J.*, Nov. 23, 1939, p. 46.

TABLE 17.—RANGE OF PHYSICAL PROPERTIES OF LUBRICATING OILS

Name of oil	Used for	A.P.I.°	Viscosity at 100	Viscosity at 210	Flash (O.C.)	Pour-point	Carbon residue
1. Light motor.......	Automobiles	21–30	150–330	43–50	300–405	0–30	0.03–0.12
2. Medium motor....	Automobiles	21–28	225–450	47–58	340–430	0–40	0.06–0.38
3. Heavy motor......	Automobiles	20–27	300–650	52–77	360–450	0–40	0.1 –1.2
4. Extra heavy motor	Automobiles	18–26	500–2,100	70–125	370–470	0–45	0.2 –2.3
5. Diesel engine......	Diesels	22–25	....	55–70	370–450	10–50	0.3 –0.8
6. Tractor...........	Tractors	22–25	....	66–155	380–500	10–50	0.4 –1.8
7. Aero.............	Airplanes	23–26	....	75–125	400–475	0–45	1.0 –2.5
8. Transmission......	Automobiles	20–23	....	90–175	440–515	40–60	2.5 –4.6
9. Cylinder (S.R.)...	Steam engines	19–27	....	90–330	415–630	35–70	1.5 –4.5
10. Engine..........	Heavy bearings	21–27	150–330	......	350–550	0–35	
11. Crank case........	Steam engines, crank case, splash, etc.	22–27	190–330	......	400–550	0–35	
12. Turbine..........	Steam turbines, dynamos	26–32	90–285	......	320–420	10–30	
13. Cold test.........	Ice machines, recoil aircraft, machine guns, etc.	25–33	50–400	......	90–450	−50 to −5	
14. Spindle, etc......	Light machines, weaving, spinning, automatics, etc.	26–35	90–150	......	340–390		
15. Black............	Rough, slow-speed bearings, crushers, etc. (cheap work)	16–28	....	95–160	375–450	15–40	
16. White............	Machines in food plants, etc.	29–32	87–140	......	290–380		

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[20] Some performance data indicate that the most valuable lubricants are removed by extensive treatment, but this is a problem that is far from settled.

[21] *Proc. A.S.T.M.*, **28,** Part 2 (1928).

that the amount formed is not directly (much less) proportional to the carbon residue. "Of course if the oils have different viscosities at the operating temperature, the one with the lower viscosity tends to pass the rings in larger quantities and thus affects the amount of carbon formation." Naphthene-base oils deposit less carbon[22] in an engine than other bases of oils, and some refiners are claiming that naphthene-base lubricating oils will clean the carbon out of an already dirty engine.

Unfortunately, even a complete laboratory examination in which all of the foregoing tests are employed does not always indicate the true usefulness[23] of an oil when in service. For this reason, a work-test[24] has been adopted by the United States Navy for evaluating an oil under conditions similar to those which it must meet in actual service. The comparison of lubricating oils given in Table 18 was obtained in engine tests conducted by Born and Harper[25] and serves to emphasize that no single type or base of oil is greatly superior to another.

In 1939 the production of lubricating oils was about 38,258,000 bbl.[26] About 57 per cent of the total domestic demand is

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[22] LIVINGSTON and GRUSE, Carbon Deposits from Lubricating Oils, *Ind. Eng. Chem.*, **21**, 904 (1929).

[23] The industry has apparently conceded that high-viscosity-index oils, such as Pennsylvania oils, are greatly superior and has attempted to make all oils meet the specifications of paraffin-base oil. Although high-index oils are necessary for certain exacting duties, the less-valued oils fill the need for a cheap grade of oil and are certainly good enough for most purposes. Doubtless the use of the so-called inferior oils is more economical for certain services than high-index oils. After all, lubrication is an economic problem, not a scientific novelty. Perhaps a comparison of oils based upon a purely cost basis, consisting of (1) cost of lubricant, (2) expenses and inconveniences involved in overhauling the engine, (3) cost of replacements and repairs directly due to a faulty lubrication, and (4) performance, may lead to a public favor of mixed- and naphthene-base oils. Without doubt the mixed-base oils do not give so much trouble by sticking valves or by hard carbon deposits. Few complete tests of this nature have been conducted, and those which are available do not definitely indicate that high-index oils are superior. Note Cross, "Handbook," *Bull.* 25, p. 426, 1928; Livingston and Gruse, *Ind. Eng. Chem.*, **21**, 904 (1929); O'Neill and McGeary, *Nat. Petroleum News*, June 11, 1930; and Born and Harper, *Oil Gas J.*, Nov. 1, 1934, p. 12.

[24] O'NEILL and MCGEARY, Evaluation of Lubricating Oils by the Work-factor Method, *Nat. Petroleum News*, June 11, 1930, p. 63.

[25] Results of Engine Tests . . . , *Oil Gas J.*, Nov. 1, 1934, p. 12.

[26] REID, G., Source and Distribution of Lubricating Oil, *Ref. Nat. Gaso. Mfr.*, May, 1931, p. 110.

TABLE 18.—ENGINE PERFORMANCE OF MID-CONTINENT, PENNSYLVANIA, AND SOLVENT REFINED LUBRICATING OILS

Regarding	3 solvent refined oils	5 Mid-Continent oils	1 Pennsylvania oil
Carbon deposits	1 better than average	4 better than average	1 worse than average
Oil consumption	1 better than average	3 better than average	1 worse than average
Gasoline consumption	2 better than average	2 worse than average*†	1 worse than average
Lubricating value	1 better than average	2 worse than average*	1 worse than average

* One test equal to average.
† One test was in error and was discarded.

used for automotive lubrication, and the rest was for industrial lubrication. The following tabulation gives interesting data (1930) regarding the kinds of crude oil used in manufacturing lubricating oils.

Type of crude	Per cent of production	Average per cent recovery from crude	Per cent of crude processed for lubricants
1. Mixed base	32	20	9.1
2. Paraffin base	30	30	100.
3. Coastal crude	31	30	32.4
4. California crude	7	20	5.

Greases and Waxes.—Greases and waxes also constitute a large group of different materials. Among the greases are recuperator, crankpin, rod, cup, graphite, driving journal compound, axle, and fiber greases. Petrolatum stock is also used in the manufacture of shoe polish, medicinal salves, hair pomades, vaseline, cosmetics, etc. Paraffin wax is used as a sealing and insulating material, in candle manufacture, as a compounding material in the manufacture of waxes and salves, and in the manufacture of wax paper and matches.

The compounding of greases, etc., is often considered as an art, and few "grease-makers" use the same process of manufacture. Greases may be grouped into three classes.[27]

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[27] SIMPSON and WELCH, Manufacture of Grease, *Ref. Nat. Gaso. Mfr.*, March, 1931, p. 77.

1. Admixtures of mineral oil and solid lubricant. Some of the common solid lubricants are graphite, mica, talc, sulfur, and asbestos fiber. These greases are invaluable in the lubrication of ill-fitting machine parts functioning under heavy or intermittent loads. Examples of this type are tractor-roller lubricants, lubricants for concrete mixers, ditch-digging equipment, and railroad-car unloading devices.

2. Blends of residuum, waxes, uncombined fats, rosin oils, and pitches. This group is particularly suited to the lubrication of rock bits, steel cables, water pumps, dredges and chains, and gears operating under water or under exposed weather conditions.

3. Soap-thickened mineral oils. Common thickeners are sodium, calcium, aluminum, and lead soaps. The soaps of these metals are prepared by saponification of a fatty glyceride of either animal or vegetable origin. This group is widely useful because a large variety of different-consistency greases can be produced by selecting various metallic soaps, fatty glycerides, and mineral oils.

There are also three general bases[28] used for manufacturing the extreme-pressure (E.P.) lubricants now used widely for differential, transmission, and general gear lubrication.

1. Blends of saponifiable oil containing chemically combined sulfur with a suitable lubricating oil—or mineral oils to which flowers of sulfur has been added.

2. Blends of a sulfur chloride-treated saponifiable oil base and a lubricating oil of suitable viscosity—or chlorine combined directly with chosen mineral-oil fractions.

3. Lubricants containing lead soaps of fatty or naphthenic acids and sulfur. These may contain sulfur that has been added or only the sulfur that is naturally present in the mineral oil.

The general theory regarding sulfur and chloride lubricants is that iron sulfide or iron chloride should be formed on the surfaces of the bearing or shaft and that the films of these materials are responsible in part for good lubrication. Thus, the extreme-pressure lubricants are somewhat corrosive and probably should not be used on bearings that contain copper.

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[28] Ebaugh, I. A., Service Tests Must Determine Value of Extreme Pressure Lubricants, Part 2, *Nat. Petroleum News*, Jan. 15, 1936, p. 26.

The S.A.E. recommends the following transmission oils:

S.A.E. No.	Saybolt Universal viscosity	Special pour-point
80	Max. of 100,000 at 0°F.	−20
90	80 to 1500 at 100°F.	0
140	120 to 200 at 210°F.	35
250	Min. of 200 at 210°F.	

The S.A.E. 250 transmission oil is used primarily for trucks and busses. Although these oils are referred to as transmission oils, the grading system is also employed in specifying rear-axle, steering, and other greases.[29]

Paraffin wax is marketed according to the melting-point. The melting-point ranges from 105 to 140°F. Crude wax is sold in two common grades having melting-points of 118 to 120°F. and 124 to 126°F. Crude wax is used in the manufacture of matches, as a stuffing or loading material for leather goods, and in the textile industry for softening and lubricating yarn during winding. *Refined wax* must be free from odor or taste, and usually a white wax is required. A large quantity of refined wax is used in the water-proofing of food containers. It is also used industrially as a lining for vats, tubs, containers, etc., in food-manufacturing plants. The highest grade of common wax, having a melting-point of approximately 140°F., is used for the manufacture of wax paper, and the most common low-melting (110 to 112°F.) wax is used in manufacturing matches. In the past high-melting-point waxes have been manufactured from East Indian petroleum, but more recently special waxes having melting-points exceeding 190°F. have been manufactured in the United States by solvent dewaxing or crystallization of the so-called amorphous waxes contained in petrolatum stock.

Residues.—The residual petroleum products usually do not command a high market price. Often they are merely by-products of the regular refining operation. Some of the residual products are residual fuel oil, fuel oil for diesel power engines, road oil, spray oil, coke, and paving, roofing, or paint asphalts.

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[29] THOMPSON, J. W., varied E.P. Lube Specifications Complicate Servicing Cars, *Nat. Petroleum News*, Sept. 30, 1936, p. 36.

Typical residual fuel oils exhibit the properties shown in Table 19. The first and last of these are the 1940 commercial standard, whereas the second and third were used in 1933.[30]

TABLE 19.—RESIDUAL FUEL OILS

Fuel oil	Flash-point, deg. F.	Water and sediment, maximum per cent	Pour point, maximum, deg. F.	Maximum viscosity, sec.
1. Low viscosity	130	1	..	50 Saybolt at 100°F.
2. Medium viscosity	150–250	1	15	125 Saybolt at 100°F.
3. Bunker B	150	1	..	100 Furol at 122°F.
4. Bunker C	150	2	..	300 Furol at 122°F.

All of the oils must be free from grit, acid, and fibrous or other foreign matter that might clog or injure burner valves. The main difference in the specifications of the three government fuel oils is the viscosity. Residual fuel oils usually have a flash-point (O.C.) higher than 200°F., a Furol viscosity of about 100 sec. at 122°F., a pour-point not exceeding 40°F., and the gravity ranges between 6 and 27 A.P.I. Sulfur is usually limited to 1.5 per cent, and water and sediment to 1 per cent. Cracked fuel oils are desirable[31] as fuels because they usually have a lower pour-point, lower viscosity, and a slightly higher heating value than the residues from which they are produced. However, certain cracked oils deposit carbonaceous material on steam heating-coils,[32] and hence cutter stocks having a high solvent power such as low aniline-point extracts or cracked gas oils, rather than straight-run gas oils, should be employed for reducing the viscosity of heavy, cracked fuel oils.

Petroleum coke is used commercially as follows:[33] as a refinery and commercial fuel (often powdered); in the manufacture of carbon electrodes, brushes, plates, etc.; in the manufacture of abrasives and artificial graphite; in the manufacture of calcium carbide; as a metallurgical fuel; in paints and pigments; in gas manufacture; and in the ceramics industries. The high heating value and freedom from clinker-forming substances, the small quantity of ash, and the low sulfur content of some petroleum coke make it a desirable fuel in metallurgical processes. Below are listed the average physical properties of common petroleum cokes:

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[30] *Bur. Standards C.S.* 12–40 and also *C.S.* 12–33.

[31] MORRELL and EGLOFF: The Congealing Temperature . . . of Cracked Residue, *Ref. Nat. Gaso. Mfr.*, April, 1923, p. 17.

[32] BATCHELDER, A. H., The Stability of Residual Fuels, *Oil Gas J.*, Nov. 12, 1936, p. 159.

[33] SWANSON, E. B., Petroleum Coke, *U.S. Bur. Mines, Econ. Paper* 9, 1930.

Apparent density	0.9–1.1
Structure	Cellular to granular
Color	Dark brown to grayish black

PROXIMATE ANALYSES OF PETROLEUM COKES, PER CENT*

	Cracking still	Coking still	Oven
Moisture	0.15–3.3	0.3–1.8	0.3–1.1
Volatile matter	8–18	2–13	1–7.4
Fixed carbon	79–92	85–96	92–99
Ash	0–1.6	0.5–1.2	0.2–1.8
Sulfur	0.2–4.2	0.5–1.2	0.8–1.5
Heating value, B.t.u. per lb.	15,300–16,400	14,500–15,500	14,400–14,700

* "Science of Petroleum," Vol. IV, p. 2774, Oxford University Press, New York, 1938.

In the past the term *road oil* has been used carelessly by the refiner. The term has been used to designate any fluid residual oil for the purpose of "laying" the dust on dirt or gravel roads. Gradually the meaning of the term road oil has been revised so that now it refers to the more viscous grades of oil. These oils contain a high percentage of solid asphalt, and upon exposure the more volatile portion of the oil evaporates, leaving a solid tar which acts as a binding material for earth or aggregate. *Cutback* road oils are manufactured by blending gas oil and asphalt. Table 20 indicates the ranges of composition and properties of road oils. The many state specifications vary so widely that only the limits of the properties are given in Table 20. The table should not be used as a set of specifications.

The United States Federal Specifications for petroleum asphalt cover three main groups of penetration as shown below. In addition to the properties listed, the asphalts must not foam when heated to 347°F., the minimum flash-point is 347°F.,

TABLE 20.—PROPERTIES OF ROAD OILS

Property	Usual range	Limiting property which may be difficult to obtain
Specific gravity at 77°F.	0.95–1.03	0.95+
Asphalt content (100 penetration at 77°F.)	40–85 per cent	85+
Asphalt content (80 penetration at 77°F.)	35–94 per cent	94+
Furol viscosity at 210°F.	Wide range	
Solubility in carbon disulfide	99–99.5	99.5+
Percentage asphaltenes	4–15	Either extreme
Flash-point (O.C.)	120–400	400+
Evaporation loss:		
Residue oils	1–15 per cent	1−
Cutback oils	2–40 per cent	2−
Ductility of asphalt content	1–100	100+

the loss upon heating at 163°F. for 5 hr. must not exceed 1 per cent (and 60 per cent of the residue must have the same penetration as the original sample), and the solubility in carbon disulfide must be over 99.5 per cent.

	100–150 penetration	50–100 penetration	40–50 penetration
Specific gravity, min	1.0	1.0–1.01	1.01
Softening point, deg. F	95–131	104–140	113–149
Ductility, min	......	40	40

The A.S.T.M.[34] specifies the properties of emulsified asphalts (D397-39, D398-39, D399-39, D401-36T). Table 21 indicates other important properties of asphalts.

Asphalt finds many uses other than as a road or roofing material. Among these are water-proofing of concrete and reservoirs, water-proofing paints, rubber filler or substitutes, saturant for felting, as a briquette binder, and in the prevention of corrosion. In 1930 the sales of petroleum asphalt in the United States amounted to 3,326,378 tons valued at $35,380,620.

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[34] Petroleum Products and Lubricants, A.S.T.M., 260 South Broad Street, Philadelphia, Pa., yearly.

TABLE 21.—ASPHALT MATERIALS

Materials	Penetration at 77°F.	Ductility at 77°F.	Melting point, Ring and Ball
Paving binders:			
Mastic foot pavements and floors	10–15	.....	180–220
Asphalt blocks	10–25	20+	
Sheet asphalt pavement	25–40	40+	105–140
Grout filler	40–70	50+	113–140
Grout filler (blown type)	30–50	3+	150–230
Asphalt concrete (aggregate sand, etc.)	30–70	45+	113–150
Asphalt macadam	70–150	90+	104–113
Roofing asphalts:			
Saturant for felt or paper	75–140	100+	110–120
Heavy saturant for felt and rugs	28–32	40+	140–150
Roof coatings (blown)	10–50	1+	160–260
Sealing:			
Pipe sealing (sewers, etc.)	40–60	1+	200–225
Pipe coatings	10–15*	1+	200–215
Water-proofing	25–50	15+	140–170

* Consistency.

Petroleum Specialties.—During the last decade refiners have developed a large number of specialty products. More and more research work on the constitution of petroleum is being conducted, and soon we may expect to have a purely chemical petroleum industry for the manufacture of chemical products that are far different from the petroleum products of today.

Among the many special products from petroleum, natural gas, etc., are the following: liquefied petroleum gas for domestic use, medicinal white oil, medicinal and dental wax, printer's ink, shoe polish, insecticides, furniture and automobile polish, dripless oils, and brick molding oils. The field of petroleum chemistry has hardly been touched, and among the many possible petroleum derivatives are explosives; dye intermediates; pure hydrocarbons (paraffin, naphthene, and aromatic); soaps; antiseptics; anesthetics; wood preservatives; antifouling paints for ship bottoms; chemical alcohols; lacquers; varnishes; chlorinated products such as chloroform, carbon tetrachloride, and alkyl chlorides; organic acids; refrigerants; and rubber substitutes. Indeed, the possibilities are so many that the products cannot be predicted.

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CHAPTER X

FLUID MECHANICS

The processing of petroleum consists primarily of three operations—heating, distillation, and transferring fluids. In spite of the basic importance of a knowledge of pumping, the refinery industry has not greatly enriched our knowledge of hydraulics. Rather, the refiner has turned to the comprehensive literature on the hydraulics of water and has adapted this information to the handling of petroleum. Although this practice has not led to serious difficulties, two important differences between oil and water must be recognized: oils exhibit a wide range of viscosity, and they are sensitive to the action of heat.

Mechanism of Fluid Flow.—Flow within a tube or pipe is divided into two types of motion: streamline flow and turbulent flow. Streamline flow occurs at low velocities, whereas turbulent flow occurs at higher velocities. In streamline flow, through a circular conduit, the fluid travels as a series of cylinders which slip past one another. Flow at the center of the pipe progresses at the greatest velocity, and the cylindrical film at the wall is almost stagnant. The wall of a pipe is relatively rough compared with the thickness of the film, and the irregularities in the surface are effective in trapping part of the fluid and retarding its flow. Reactions are communicated to the body of the fluid by the viscosity or drag between particles. In small tubes or containers the condition of the surface is vitally important, but in conduits having diameters of 6 to 12 in. the condition of the surface is much less important.[1] The condition of the surface is more important at streamline conditions than at turbulent conditions.

Friction Losses.—When a fluid moves through a constriction in the passage through which it flows, a loss of energy occurs. Loss is caused by the impact of fluid particles upon the walls of the conduit and by friction between particles of fluid as they move past one another. Fanning's equation for the pressure loss due to turbulent flow within a circular conduit may be expressed in English units as follows:

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[1] Heltzel, W. G., Fluid Flow and Friction in Pipe Lines, *Oil Gas J.*, June 5, 1930, p. T203.

$$\Delta P_f = \frac{0.323 fsu^2L}{D}; \qquad \text{or} \qquad \frac{1.488}{100{,}000}\frac{Q^2}{D^5} fsL \tag{6}$$

where ΔP_f = pressure loss, lb. per sq. in.
s = sp. gr. referred to water at 60°F.
u = velocity, ft. per sec.
L = equivalent length of pipe, ft.
D = diameter of pipe, in.
Q = discharge, gal. per hr.
f = friction factor, a function of Dus/z (Fig. 53).
z = absolute viscosity, centipoises.

roughout years of industrial development this equation has been found to be valid for the flow of all kinds of fluids in circular conduits. Comprehensive experimental data for sections other than circular are not available. However, the friction loss for other sections is usually computed by using the hydraulic radius

$$\Delta P_f = \frac{0.08075 fsu^2L}{m} \tag{7}$$

The hydraulic radius m is defined as the cross-sectional area divided by the wetted perimeter.

The equivalent length L is equal to the total length of straight pipe plus the lengths of pipe that are equivalent to the restrictions caused by elbows, valves, bends, etc. Equivalent lengths are usually expressed as diameters of straight pipe. Table 22 shows equivalent lengths for fittings at turbulent conditions of flow. The data by Walker, Lewis, McAdams, and Gilliland[2] are for all fluids, whereas the data of F. M. VanDeventer[3] are for somewhat viscous fluids (not water). VanDeventer[3] also states that for flanged fittings the equivalent lengths should be decreased by factors of 0.75 to 0.96. Equivalent lengths for viscous or streamline flow are so small that they are usually neglected.[4] Fanning's equation is not valid for the flow of gases if the pressure-drop is more than 10 per cent of the downstream pressure.

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[2] "Principles of Chemical Engineering," 3d ed., p. 86, McGraw-Hill Book Company, Inc., New York, 1937.

[3] Catalogue 89 of Walworth Company.

[4] WILSON, MCADAMS, and SELTZER, *Ind. Eng. Chem.*, **14**, 105 (1922).

The Fanning equation is usually used for both turbulent and streamline conditions, but the friction factor is much larger for streamline conditions (Fig. 53). The Poiseuille equation, which does not involve a friction factor, may also be used for streamline flow.

TABLE 22.—EQUIVALENT LENGTHS OF FITTINGS FOR TURBULENT FLOW

Fittings	Nominal size, in.	Diameters of straight pipe	
		McAdams	Walworth
90-deg. elbows	1-2½	30	22
	3-6	40	22
	7-10	50	22
Return bends:			
Streamline	2-4	40*	
Square block	2-4	80*	
Close	All sizes	....	54
Pipe bends	90 deg., radius of center-line curve equals 2-8 diameters	10	
Tees	1-4, through side outlet	60	54
	All sizes, straight through	....	18
Valves:			
Globe	1-2½	45	240
	3-6	60	240
	7-10	75	240
Gate	1-2½	12	9
	3-6	16	9
Angle	All sizes	....	120
Entry†	Sharp edge, flush with wall	20	
	Sharp edge, extending into reservoir	40	
	Rounded	None	
Meters		135-600	

* General refinery practice for pipestill bends.

† These losses can be computed more accurately by enlargement loss equations.

The Friction Factor.—The friction factor *f* in Fanning's equation has always been troublesome to engineers. Reynolds in 1883 recognized the relation between the friction factor and the dimensionless group *Dus/z*, but extensive data with which to check the relationship were not available until later. The

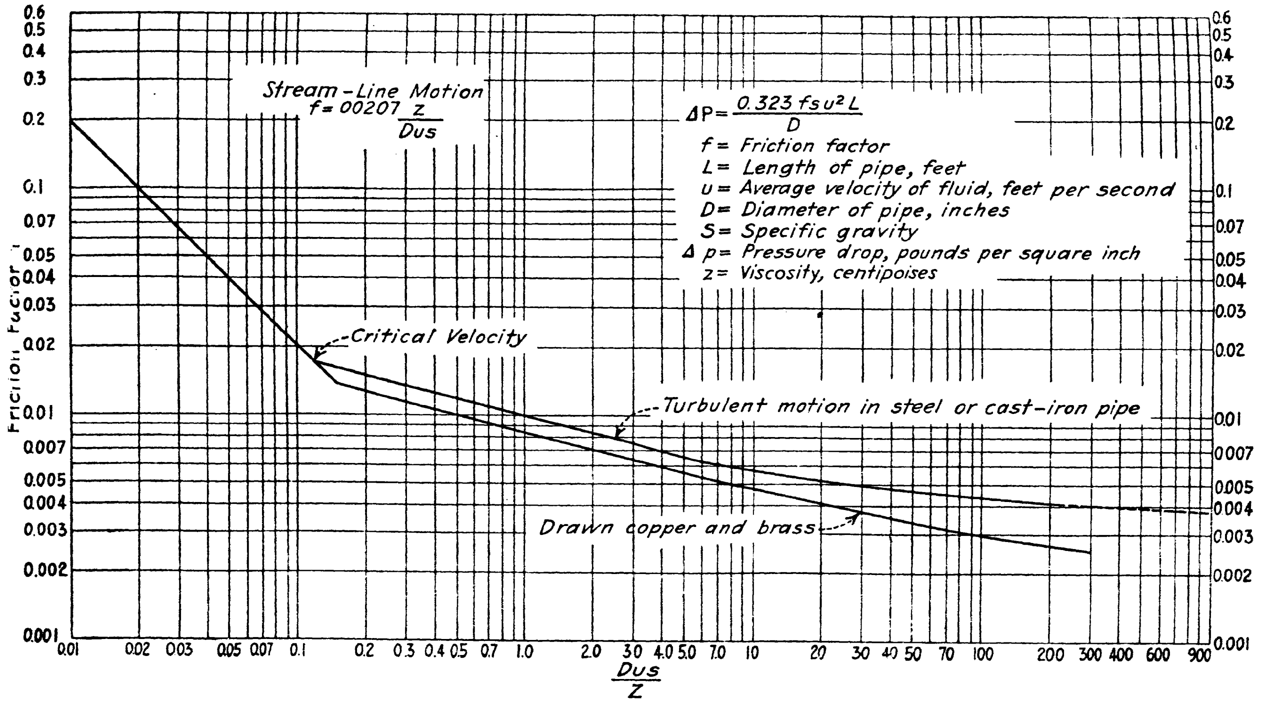

FIG. 53.—Friction factor for isothermal conditions as a function of Reynolds' criterion.

group Dus/z is known as Reynolds' criterion. This factor can sometimes be handled more easily as $0.00682Qs/Dz$, in which Q equals gallons per hour.

The relation between the friction factor and Dus/z for an isothermal system is shown in Fig. 53. Keevil and McAdams[5] have determined the effect of heating or cooling on the friction factor.

The relation shown in Fig. 53 has been repeatedly checked[1,4,6,7] by numerous experimenters using a variety of materials, including water, air, natural gas, steam, oils, and solutions. Many empirical formulae for the pressure required to pump oil have been proposed. When these formulae are analyzed and inserted in the Fanning equation, they yield friction factors that are in close agreement with those given in Fig. 53.[8] In general, the friction factor should be slightly higher than that shown in Fig. 53 for small pipe sizes (less than 1½ in.) and slightly less for pipe exceeding 8 in. in diameter. The value of Dus/z when pumping natural gas in commercial lines is very high[7] and cannot be found on Fig. 53. The value of the friction factor is between 0.0033 and 0.0045 for pumping natural gas at high pressures.

Condition of Pipe Surface.—The friction factors shown in Fig. 53 are for commercially clean new pipe and are smaller than those usually obtained in practice. The smaller the pipe the greater is the effect of the surface in increasing the friction loss. For very large pipe the condition of the surface may be neglected entirely. The friction loss in old or corroded small pipes may be twice as great as for new clean pipe. The factors shown in Table 23 were published by F. L. Snyder.[9]

Viscosity of Liquid-vapor Mixtures.—The viscosity of mixtures of oil vapor and oil is a particularly pertinent problem because such mixtures are so frequently handled in the refinery. Whenever a material is continuously heated in exchangers or tubular heaters, vaporization occurs, and the viscosity of the resulting mixture of vapor and oil governs the pressure-drop. Apparently only one article that pertains directly to this important problem has been published. Uren[10] has conducted experiments regarding

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[5] *Chem. Met. Eng.*, **36**, 484 (1929).

[6] McAdams and Sherwood, Flow of Air and Steam in Pipes, *Mech. Eng.*, October, 1926.

[7] Berwald and Johnson, Factors Influencing Flow of Natural Gas . . . , *U.S. Bur. Mines, Repts. Investigations Serial* 3153, 1931.

[8] The equations and data of Danforth, Twel, Bell, and McGregor have been checked in this manner.

[9] *Heating, Piping and Air Conditioning*, January, 1935.

TABLE 23.—EFFECT OF SURFACE CONDITION

Condition or Kind of Pipe Surface	Correction Factor for Condition of Surface
Brass, copper, or lead (smooth)	0.9
Steel, cast iron, or corrosion-resistant metal (new)	1.0
Wood pipe or concrete lined (smooth)	1.2
Riveted steel or *old* cast iron	1.4
Vitrified or *old* steel pipe	1.6
Old riveted steel pipe	2.0
Badly tuberculated pipe	2.5

the mechanics of flow in columns of mixtures of oil and air. By assuming that Reynolds' criterion was valid for such a case, he

TABLE 24.—STANDARD FULL-WEIGHT WROUGHT-IRON AND STEEL PIPE

Nominal diameter, in.	Diameter, approx. internal, in.	Diameter, external, in.	Thickness, in.	Circumference, in.		Transverse internal area, sq. in.	Ft. of pipe per sq. ft. of external surface	Nominal weight per ft.-lb.
				Internal	External			
1/8	0.27	0.405	0.068	0.85	1.27	0.06	9.44	0.24
1/4	0.36	0.54	0.083	1.14	1.70	0.10	7.08	0.42
3/8	0.49	0.675	0.091	1.55	2.12	0.19	5.66	0.57
1/2	0.62	0.84	0.109	1.95	2.63	0.30	4.55	0.85
3/4	0.82	1.05	0.113	2.59	3.30	0.53	3.64	1.13
1	1.05	1.315	0.134	3.29	4.13	0.86	2.90	1.68
1 1/4	1.38	1.66	0.140	4.34	5.22	1.50	2.30	2.27
1 1/2	1.61	1.9	0.145	5.06	5.97	2.04	2.01	2.72
2	2.07	2.375	0.154	6.49	7.46	3.36	1.61	3.65
2 1/2	2.47	2.875	0.204	7.75	9.03	4.78	1.33	5.79
3	3.07	3.5	0.217	9.63	11.00	7.39	1.09	7.57
3 1/2	3.55	4.0	0.226	11.15	12.57	9.89	0.96	9.11
4	4.03	4.5	0.237	12.65	14.14	12.73	0.85	10.79
6	6.07	6.625	0.280	19.05	20.81	28.89	0.58	18.97
8	8.07	8.625	0.276	25.35	27.10	51.15	0.44	24.69
8	7.98	8.625	0.322	25.07	27.10	50.02	0.44	28.55
10	10.19	10.75	0.278	32.01	33.77	81.55	0.36	31.20
10	10.14	10.75	0.306	31.86	33.77	80.75	0.36	34.24
10	10.02	10.75	0.366	31.47	33.77	78.82	0.36	40.48
12	12.09	12.75	0.328	37.98	40.06	114.8	0.30	43.77
12	12.00	12.75	0.375	37.70	40.06	113.1	0.30	49.56

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[10] UREN, GREGORY, HANCOCK, and FESKOV, Flow Resistance of Gas Oil Mixtures, *Oil Gas J.*, Oct. 3, 1929, p. 148.

was able to compute values of the viscosity of these mixtures. The viscosities that he obtained in this manner were not a simple function of the viscosity of the gas and of the oil but were approximately a linear function of the arithmetic mean density.[11] The mechanics of fluid flow indicates that the viscosity of the liquid will be more important than the viscosity of the gas in governing the behavior of the mixture. The liquid will be thrown to the walls of the conduit and will not travel at the average velocity of the mixture. Likewise the specific gravity used in determining the friction factor should be nearly the gravity of the oil, but the specific gravity used in the Fanning equation should be the gravity of the mixture.

Example 20. Friction Loss in an Oil Line.—One thousand six hundred gallons per hour of a 15 A.P.I. ($s = 0.966$) fuel oil at a temperature of 200°F. is to be pumped through a distance of 1,700 ft. in a 3-in. well-insulated pipeline. Two gate valves and six elbows are in the line, and the oil enters a tank through a sharp-edge entry flush with the side of the tank. The Saybolt viscosity of the oil is 300 at 210°F. What is the total friction loss in the line? Assume no change in temperature.

The viscosity of the oil at 200°F. (Fig. 48) is approximately 80 centipoises. The specific gravity at 200°F. (Fig. 43) is 0.916. The 1,600 gal. is the volume at 60°F.

$$\text{Volume at 200°F.} = 1{,}600 \times \frac{0.966}{0.916} = 1{,}688 \text{ gal. per hr.}$$

$$\text{Velocity} = \frac{\dfrac{1{,}688 \times 231}{3{,}600}}{\dfrac{(3.07)^2 \times 3.14}{4}} \times \frac{1}{12} = 1.21 \text{ ft. per sec.}$$

L, the equivalent length (Table 22):

Straight pipe .... 1,700 ft.

Elbows .... $\dfrac{6 \times 40 \times 3.07}{12} = 61.4$

Gates .... $\dfrac{2 \times 16 \times 3.07}{12} = 8.2$

Entry .... $\dfrac{20 \times 3.07}{12} = 5.1$

1,774.7 ft. = total equivalent length

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[11] According to the data, the viscosity is related to the density approximately as follows: $z = -0.00055 + 0.00032s$. Doubtless this relation is not of a general nature and is not valid for other gases than air and for other oils than the one that they studied. The relation holds between limits of 24 and 120 cu. ft. of air per gallon of oil.

sing Fanning's equation, Eq. (6):

$$\frac{Dus}{z} = \frac{3.07 \times 1.21 \times 0.916}{80} = 0.043$$

The friction factor f from Fig. 53 = 0.047

$$\Delta P_f = \frac{0.323 \times 0.047 \times 0.916\,(1.21)^2 \times 1{,}774.7}{3.07} = 11.82 \text{ lb. per sq. in. for clean new pipe}$$

Check with the equation

$$\Delta P_f = \frac{1.488}{100{,}000}\frac{Q^2}{D^5}fsL$$

$$\Delta P_f = \frac{1.488 \times (1{,}688)^2 \times 0.047 \times 0.916 \times 1{,}774.7}{100{,}000 \times 273} = 11.87$$

Example 21. Friction Loss in Vapor Line.—Four thousand pounds per hour of a 55 A.P.I. naphtha vapor at a temperature of 300°F. passes through a 4-in. vapor line that is 130 ft. long. The molecular weight is 110. The pressure is 5 lb. gage. What is the pressure-drop?

Volume of vapor

$$\frac{4{,}000}{110} \times 379 \times \frac{760}{520} \times \frac{14.7}{19.7} = 15{,}000 \text{ cu. ft. per hr.}$$

Viscosity at 300°F.:

Critical temperature (Fig. 35) = 575°F.
Critical pressure (Fig. 42) = 450 lb. per sq. in. abs.
Reduced temperature $= \frac{300 + 460}{575 + 460} = 0.735$
Reduced pressure $= {}^{20}\!/_{450} = 0.045$ approx.
Viscosity (Fig. 49) = 0.008 centipoise
Specific gravity $= \frac{4{,}000}{15{,}000 \times 62.4} = 0.00427 = s$

$$u = \frac{15{,}000}{3{,}600} \times \frac{144}{12.73} = 47.0 \text{ ft. per sec.}$$

$$\frac{Dus}{z} = \frac{4.03 \times 47 \times 0.00427}{0.008} = 101.0$$

$$f = 0.0044 \text{ (Fig. 53)}$$

$$\Delta P_f = \frac{0.323 \times 0.0044 \times 0.00427 \times (47)^2 \times 130}{4.03} = 0.433 \text{ lb. per sq. in.}$$

Other Pressure Losses.—The losses due to increasing or decreasing the cross-sectional area of a conduit suddenly are sometimes relatively large. The loss due to a sudden enlargement of the cross section may be expressed as follows:

$$\Delta h_e = \frac{(u_2 - u_1)^2}{2g}; \qquad \text{or} \qquad \Delta P_e = 0.00673s(u_2 - u_1)^2 \qquad (8)$$

where Δh_e = pressure-drop expressed as ft. of fluid.
ΔP_e = pressure-drop, lb. per sq. in.
s = sp. gr.
u_2 = velocity, ft. per sec. at smaller section.
u_1 = velocity, ft. per sec. at larger section.

The loss due to a sudden contraction in the cross section is

$$\Delta P_c = 0.00673 k s u_2^2 \tag{9}$$

where P_c = pressure drop, lb. per sq. in.
k = a constant (Fig. 54).
u_2 = velocity, ft. per sec. at the smaller section.

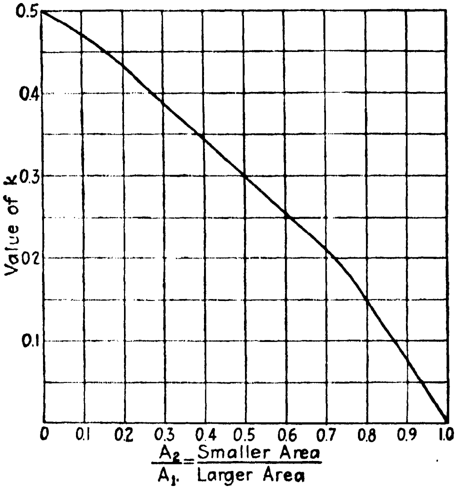

Fig. 54.—Constant for contraction losses.

Example 22. Contraction and Enlargement Losses.—*A*. Sixteen hundred gallons per hour of a 15 A.P.I. oil at a temperature of 60°F. is pumped through a 3-in. pipeline. A contraction to a 1-in. pipe occurs. What is the loss in pressure due to the contraction?

$$\Delta P_c = 0.00673 k s u_2^2$$

$$u_2 = \frac{\dfrac{1{,}600}{3{,}600 \times 7.48}}{0.86/144} = 9.95 \text{ ft. per sec. (downstream)}$$

$$\text{Ratio of } \frac{A_2}{A_1} = \frac{0.86}{7.39} = 0.116$$

k from Fig. 54 = 0.465

$\Delta P_c = 0.00673 \times 0.465 \times 0.966 \times (9.95)^2 = 0.299$ lb. per sq. in.

B. The oil then flows back to a 3-in. pipe from the 1-in. pipe. What is the loss in pressure?

$$u_2 = 9.95 \text{ (upstream)}$$
$$u_1 = 0.116 \times 9.95 = 1.15 \text{ ft. per sec. (downstream)}$$
$$\Delta P_e = 0.00673(9.95 - 1.15)^2 \times 0.966 = 0.503 \text{ lb. per sq. in.}$$

Weirs.—In refinery design the two most important weirs are the rectangular or suppressed weir and the V-notch weir. Both are used in the design of the overflow dams in bubble-towers. The formula for flow over a rectangular weir is

$$Q = 3L(h)^{3/2} \tag{10}$$

where Q = quantity of liquid, gal. per min.
L = perimeter of weir, in.
h = effective head above weir, in.

Francis (1851), Hamilton Smith (1886), and Bazin (1888) suggest constants between 3.33 and 3.7 for water, but the value of 3 seems to represent more accurately the behavior of petroleum oils. The constant holds only up to heads of 5 or 6 in. and perimeters of 24 in. The formula for the triangular weir having an angle of 90 deg. is

$$Q = 2.3L(h)^{5/2} = 1.155L(h)^{3/2} \tag{11}$$

Triangular weirs are useful if the capacity of a rectangular weir must be increased without increasing the head or the perimeter.

CHAPTER XI

COMBUSTION

The generation of power and the liberation of heat are important operations in almost all industries. The generation of heat in the petroleum industry is a somewhat different problem from that in other industries because fuel is abundant and cheap and because petroleum, the feed-stock, is affected by high temperatures.

Heating Value.—The amount of heat liberated when a unit quantity of a fuel is burned is called the heating value or heat of combustion. The heat liberation, when 1 lb. of a fuel at 60°F. is burned and the products of combustion are cooled to 60°F., is called the *net heating value.* If the products are cooled to 60°F. and in addition the water vapor in the flue gas is condensed, the *gross* or *high heating value* is obtained. In most industrial processes the water vapor contained in the stack or flue gases is not condensed, and hence the most logical basis for the design of equipment is the net heating value. Continental engineers use the net heating value, but American engineers usually base their computations on the gross heating value. The reason for the general use of the gross heating value is probably due to the fact that the gross heating value is obtained in the laboratory directly whereas a correction must be applied to obtain the net heating value.

The heat that is evolved when 1 lb. of water is condensed at 60°F. is 1058.2 B.t.u. or for 1 cu. ft. of water vapor (measured at 60°F.) 50.3 B.t.u. The net heating value can be computed from the gross heating value by subtracting the quantity of heat that is required to condense the water vapor in the flue gas.

Example 23. Calculation of Net Heating Value.—What is the net heating value of methane expressed as B.t.u. per cubic foot?

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$

One cubic foot of methane burns and produces 2 cu. ft. of water vapor. The gross heating value of methane = 1009 (Table 26).

$$\text{Net heating value} = 1009 - 2 \times 50.3 = 908.4 \text{ B.t.u. per cu. ft.}$$

Compute the net heating value of fuel oil 1 in Table 25 (page 176)

$$H_2 + \tfrac{1}{2}O_2 = H_2O$$

The molecular weight of hydrogen is 2 and of water 18. Two pounds of hydrogen burns, yielding 18 lb. of water.

$$\text{Water produced per lb. of fuel} = 0.12 \times \tfrac{18}{2} = 1.08 \text{ lb.}$$

Gross heating value from Table 25 is 19,376 B.t.u. per lb.

$$\text{Net heating value} = 19{,}376 - 1.08 \times 1058.2 = 18{,}234 \text{ B.t.u. per lb.}$$

Refinery Fuels.—The heating value of petroleum-oil fractions increases with gravity as shown in Fig. 50 (page 128). Table 25 indicates the characteristics of the solid and liquid fuels that are used in the refinery. In this table the heating value, pounds air per pound fuel, and the percentage of carbon dioxide were computed on the "as fired" basis. Although the heating value is of some importance in the selection of a fuel, the viscosity and atomizing properties of the oil are usually more important. Viscous fuel oils must be heated in order to obtain adequate atomization.

Natural gas and cracked gas are also used extensively as refinery fuels. Gas is more easily fired than solid or liquid fuels, but it has the minor disadvantage of producing a long flame and a flame that is often deficient in its ability to radiate heat. Some of the characteristics and combustion constants for gaseous fuels are given in Table 26. The table is for gases that contain no air or inert gases. Inert gases are usually present in amounts ranging from 1 to 10 per cent, and hence the heating values of commercial gases will range from 11 to about 206 B.t.u. lower than shown in the table. The flames produced by wet gases, particularly wet cracked gases, are almost as luminous as oil flames and are good radiators.

Combustion Reactions.—The fundamental reactions involved in combustion are shown in Table 27. If the ultimate analysis of the fuel is available, these equations are all that are required to solve many combustion calculations.

An examination of these chemical equations yields information concerning (1) the weights of materials that react and (2) the volumes of gases that react. For example, reaction 1 indi-

TABLE 25.—REFINERY FUELS

Fuel	A.P.I.	H_2O	Ultimate composition					Per cent undetermined, ash, etc.	Heating Value†		Lb. air per lb. fuel at 0 per cent excess air*	Per cent CO_2 at 0 per cent excess air*
			C	H_2	S	O_2	N_2		Gross	Net		
1. Mid-Continent topped crude	27.1	....	86.1	12.0	0.35	1.1		0.45	19,376	18,241	14.17	15.7
2. Topped crude, Calif	26.2	0.89	85.8	12.09	1.19	....	....	0.04	19,053	18,001	14.12	15.65
3. Mid-Continent topped crude	25.5	....	86.5	12.38	0.46	....	....	0.76	19,182	18,002	14.1	15.6
4. Mid-Continent topped crude	25.3	....	86.4	12.38	0.46	....	....	0.46	19,353	18,173	14.3	15.6
5. Mid-Continent topped crude	25.1	0.33	86.2	12.39	0.39	....	....	0.69	19,256	18,076	14.1	15.6
6. Topped crude, Ky	24.4	....	87.1	12.53	0.22	....	....	0.15	19,358	18,168	14.35	15.6
7. Mid-Continent residuum	22.0	0.05	87.4	11.1	0.42	....	....	1.03	18,778	17,723	14.0	16.0
8. Topped crude, Calif	18.7	0.05	85.6	11.4	1.6	....	....	1.35	18,607	17,522	14.0	15.8
9. Residual fuel oil, Calif	16.5	0.05	87.5	10.17	1.14	....	....	1.14	18,319	17,351	13.7	16.4
10. Fuel oil, Calif	15.6	....	84.0	12.6	0.75	2.55		0.10	18,910	17,720	14.25	15.4
11. Residual fuel oil, Ky	15.2	0.05	88.7	10.23	0.3	....	....	0.72	18,651	17,677	13.8	16.4
12. Mid-Continent residuum	14.3	0.05	87.6	10.27	0.70	....	....	1.38	18,454	17,479	13.7	16.4
13. Mexican crude	13.6	1.85	83.7	10.2	4.15	....	....	0.10	18,710	17,767	13.4	16.2
14. Cracked fuel oil, Calif	11.3	0.3	86.5	10.04	1.49	....	....	1.67	18,088	17,128	13.5	16.4
15. Mid-Continent cracked residuum	10.7	....	88.5	9.92	0.77	....	....	0.81	18,293	17,349	13.65	16.5
16. Mid-Continent cracked residuum	9.2	0.4	88.4	9.95	0.68	....	....	0.81	18,274	17,324	13.7	16.6
17. Mid-Continent cracked residuum	8.6	....	88.9	9.8	0.56	....	....	0.74	18,277	17,345	13.7	16.6
18. Mid-Continent residuum	8.1	0.25	88.5	9.07	0.67	....	....	1.51	18,077	17,212	13.4	16.9
19. Cracked residuum, Calif	8.0	0.05	88.3	9.5	1.2	....	....	0.95	18,084	17,179	13.5	16.7
20. Residual fuel oil, Calif	7.6	0.10	87.5	9.38	1.37	....	....	1.65	17,970	17,075	13.4	16.8
21. Cracked residuum, Ky	3.3	....	90.6	8.49	0.41	....	....	0.50	17,837	17,030	13.4	17.1
22. Bituminous coal, Pa	....	2.5	77.8	4.8	1.2	6.2	1.5	6.0	13,997	13,543	10.4	18.6
23. Bituminous coal, Mo	....	2.6	72.6	4.6	1.8	6.3	1.2	10.9	13,533	13,098	9.7	18.6
24. Petroleum coke	....	1.2	96.0	2.1	0.41	....	....	0.29	15,241	15,040	11.9	18.9

* On the "as fired" basis.

TABLE 26.—GASEOUS FUELS

Material	Mol. wt.	Density, lb. per cu. ft. at 60°F.	Analysis, volume per cent									Gross H.V., B.t.u. per cu. ft.	Cu. ft. air per cu. ft. gas at 0 per cent excess air	Per cent CO_2 at 0 per cent excess air
			CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}			
1. Methane	16	0.0422	100	...	.....	...	.....	...	.....	.....	.....	1,009	9.57	11.65
2. Ethane	30	0.0792	.....	...	100	...	.....	.....	.....	.....	.....	1,795	16.75	13.1
3. Propane	44	0.1162	.....	...	.....	...	100	...	.....	.....	.....	2,580	23.9	13.7
4. Butane	58	0.153	.....	...	.....	...	.....	...	100	.....	.....	3,350	31.1	14.0
5. Pentane	72.1	0.632*	.....	...	.....	...	.....	...	.....	100	.....	21,100†	37.9	14.2
6. Hexane	86.1	0.664*	.....	...	.....	...	.....	...	.....	.....	100	21,000†	45.5	14.3
7. Octane	100.1	0.687*	.....	...	.....	...	.....	...	.....	.....	.....	20,800†	59.8	14.47
8. Natural gas, wet	21.8	0.0577	80	...	6.6	...	6.3	...	3.7	3.0	.....	1,360	12.58	11.99
9. Natural gas, wet	20.5	0.0541	81.3	...	9.8	...	5.6	...	1.7	0.9	0.5	1,253	11.85	11.96
10. Natural gas, dry	19.5	......	85.1	...	6.1	...	7.4	...	1.2	0.1	.....	1,200	11.34	11.9
11. Natural gas, dry	18.6	0.049	86.6	...	8.6	...	3.9	...	0.7	0.2	.....	1,160	10.95	11.89
12. Natural gas, dry	17.3	0.0458	90.7	...	6.2	...	2.1	...	1.0	....	.....	1,112	10.58	11.81
13. Cracked gas, wet	35.0	0.098	34.6	1.7	21.6	4.7	17.4	3.0	7.5	5.8	3.5	2,058	19.38	12.91

* Specific gravity of liquid 60/60.

† B.t.u. per pound of liquid.

cates that 1 cu. ft. of hydrogen reacts with one-half of 1 cu. ft. of oxygen to produce 1 cu. ft. of water vapor. Likewise reaction 6 shows that one volume of methane requires two volumes of oxygen for combustion. One volume of carbon dioxide is produced, and two volumes of water vapor. Volumes are directly proportional to mols, and hence the number of mols that react are directly proportional to the number of volumes that react. The molecular weight of methane is 16 and of oxygen 32. With reference to reaction 6, 16 lb. of methane reacts with 2 × 32 lb. of oxygen to produce 44 lb. of carbon dioxide and 2 × 18 lb. of water. A knowledge of these elemental combustion reactions, along with data on specific heats of the gaseous products, constitutes the basis for almost all combustion calculations.

TABLE 27.—COMBUSTION REACTIONS

Reaction	Fuel name	Mol. wt.	Heating value, B.t.u. per lb.	Lb. air per lb. fuel, no excess
1. $H_2 + \frac{1}{2}O_2 = H_2O$	Hydrogen	2	62,000	34.8
2. $C + O_2 = CO_2$	Carbon	12	14,600	11.6
3. $C + \frac{1}{2}O_2 = CO$	Carbon	12	4,440	5.8
4. $CO + \frac{1}{2}O_2 = CO_2$	Carbon monoxide	28	10,160	2.48
5. $S + O_2 = SO_2$	Sulfur	32	4,050	4.35
6. $CH_4 + 2O_2 = CO_2 + 2H_2O$	Methane	16	23,800	17.28
7. $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$	Ethylene	28	21,600	14.81
8. $C_2H_6 + 5O_2 = 2CO_2 + 3H_2O$	Ethane	30	22,650	16.13

These reactions do not take place completely to the formation of the products indicated in Table 27 unless an excess of oxygen or air is present. The extent to which the reaction will be completed can be computed by applying the law of mass action, but such computations are of little value in commercial work. In firing a commercial furnace the use of too little excess air is evident at once by carbon monoxide or even smoke in the stack gas. Carbon monoxide is seldom found in the flue gas from oil stills because at least 30 per cent excess air is normally used in order to keep a low furnace temperature, and no carbon monoxide is produced under these conditions if effective burners are used. High furnace temperatures tend to cause the formation of coke in the tubes or still. Not many years ago furnace designers felt that 75 per cent excess air was necessary to keep the furnace cool, but modern methods of furnace design permit the use of as little as 20 per cent excess air.

The pounds of air required for the combustion of a pound of fuel can be stated as an equation by the use of Table 27. The symbols refer to the pounds of hydrogen, carbon, sulfur, and oxygen that are present in a pound of fuel.

Lb. air required per lb. of fuel (no excess) =

$$34.8H_2 + 11.6C + 4.35S - 4.31O_2 \quad (12)$$

The pounds of flue gas per pound of fuel can be obtained by adding 1 to the pounds of air per pound of fuel. The molecular weight of flue gas including the water vapor that it contains is approximately 30.

Example 24. Weight and Volume of Flue Gas.—Fuel 1 in Table 25 is to be burned with 40 per cent excess air. How many pounds of flue gas will be produced per pound of fuel, and what will the volume of the flue gas be at 600°F.?

Assume half of the 1.1 per cent of N_2 and O_2 is oxygen.

$$\text{Lb. air (no excess)} = 34.8 \times 0.12 + 11.6 \times 0.861 + 4.35 \times 0.0035 - 4.31 \times 0.0055 = 14.171$$

$$\text{Lb. air at 40 per cent excess} = 14.17 + 0.4(14.17) = 19.84$$

$$\text{Lb. flue gas} = 19.84 + 1 = 20.84$$

$$\text{Volume at 600°F.} = \frac{20.84}{30} \times 379 \times \frac{1{,}060}{520} = 536 \text{ cu. ft.}$$

Specific Heats of Combustion Products.—The heat contained in the flue gas as it enters the stack is an important item in a heat balance. Figure 55 is a chart showing the sensible heat content of the several gases that are found in flue gas. The *sensible heat content* may be defined as the amount of heat required to change the temperature of a quantity of material from one temperature to another by simple heating. No changes of state, such as vaporization or fusion, are involved.

$$\text{Sensible heat content} = W(T_2 - T_1)C_p$$

where W = lb. material (lb.-mols in Fig. 55).

T_2 = final temperature, deg. F.

T_1 = initial temperature, deg. F.

C_p = average sp. ht. at constant pressure, B.t.u. per lb. through the temperature range of T_2 and T_1.

Figure 55 is plotted on a mol basis because the diatomic gases—oxygen, nitrogen, carbon monoxide, air, etc.—can be represented by a single curve. The same applies to other groups of gases. The figure gives the number of B.t.u. required to raise the temperature of 1 lb.-mol of gas from 32°F. to the desired temperature. The upper and left scales are for temperatures up to about 150°F., and the lower and right scales are for higher temperatures.

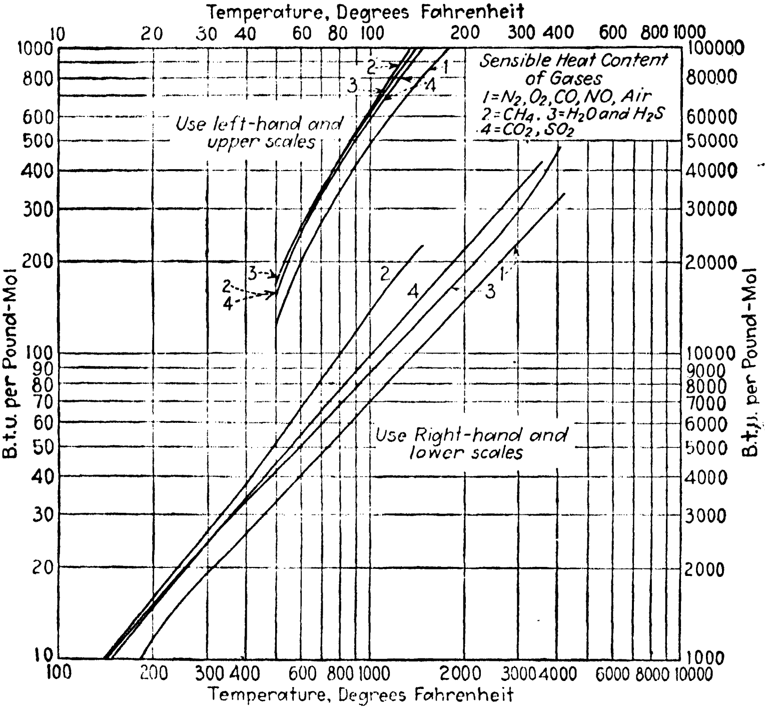

FIG. 55.—Sensible heat chart of common gases (basis 32°F.).

Example 25. Use of Sensible Heat Chart for Gases (Fig. 55).—One thousand cubic feet of a flue gas is cooled from 1000 to 100°F. Analysis of gas: CO_2, 10 per cent; H_2O vapor, 12 per cent; O_2, 3.7 per cent; and N_2, 74.3 per cent. How much heat must be removed?

$$\text{Mols } CO_2 = \frac{1000 \times 0.10}{379} = 0.264$$

$$\text{Mols } H_2O = \frac{1000 \times 0.12}{379} = 0.316$$

$$\text{Mols diatomics} = \frac{1000 \times 0.743}{379} + \frac{1000 \times 0.037}{379} = 2.057$$

SENSIBLE HEAT, B.T.U. PER MOL

Material	At 1000°	At 100°
CO_2	9850	580
H_2O	8650	610
Diatomics	7000	478

Heat removed from CO_2 = 0.264(9,850 − 580) = 2,445 B.t.u.
Heat removed from H_2O = 0.316(8,650 − 610) = 2,540
Heat removed from diatomics = 2.057(7,000 − 478) = 13,400
Total heat removed = 18,385 B.t.u.

Although heat quantities must sometimes be computed as in Example 25, the charts (Figs. 56, 57) are more convenient and are sufficiently exact for most computations. These charts are based on the net heating value because the net heating value is a more honest basis for efficiency calculations than the gross heating value. Although these charts were computed for specific fuels, they can be used for other similar fuels without great inaccuracy. They should not be used for computations with fuels that are abnormal. The subject of heat balances and material balances will be discussed more completely in Chap. XII.

Example 26. Use of Combustion Charts (Figs. 56, 57).—A 20 A.P.I. fuel oil is burned, and the gases are cooled to 300°F. The heating value of the fuel is 17,900 B.t.u. per lb. net; carbon dioxide, 13 per cent. How much heat is lost to the stack, and how many pounds of flue gas are produced? Basis: 1 lb. of fuel and 60°F. (Fig. 56).

At 13 per cent CO_2 the percentage of excess air is approximately 23. Reading between the 15 and 25 per cent excess air curves, the heat lost to the stack at 300°F. is about 6.3 per cent. This amounts to 0.063 × 17,900 or 1130 B.t.u. per lb. of fuel. Also, 14.7 lb. of flue gas or 13.7 lb. of air is required to burn 1 lb. of the fuel if no excess air is used (Fig. 56). At 23 per cent excess air the pounds of flue gas are

$$13.7 \times 1.23 + 1 = 17.9 \text{ lb. per lb. of fuel.}$$

The Burning of Oil Fuels.—In refineries or small boiler plants, fuel oil can usually be burned more efficiently than coal or gas. However, large stoker-fired coal furnaces or powdered-fuel furnaces are about as efficient as oil-fired furnaces. At low firing rates the steam-atomizing oil burner is most satisfactory, but at high firing rates the mechanical-atomizing burners are

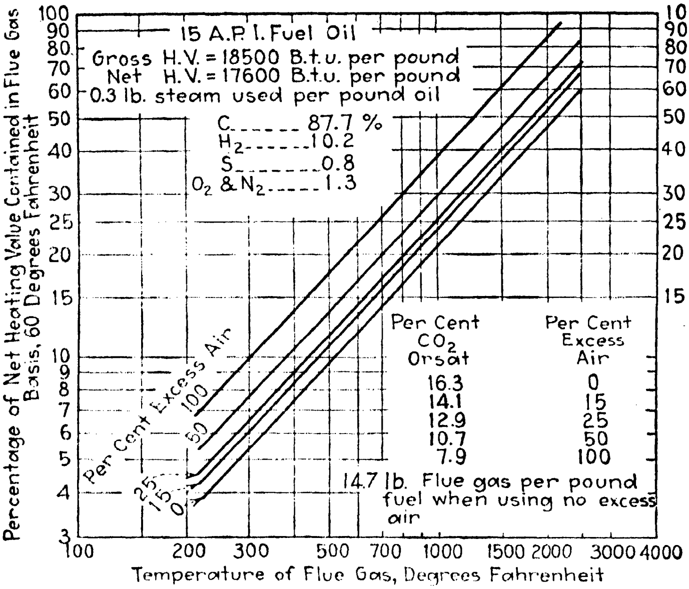

FIG. 56.—Fuel-oil combustion chart.

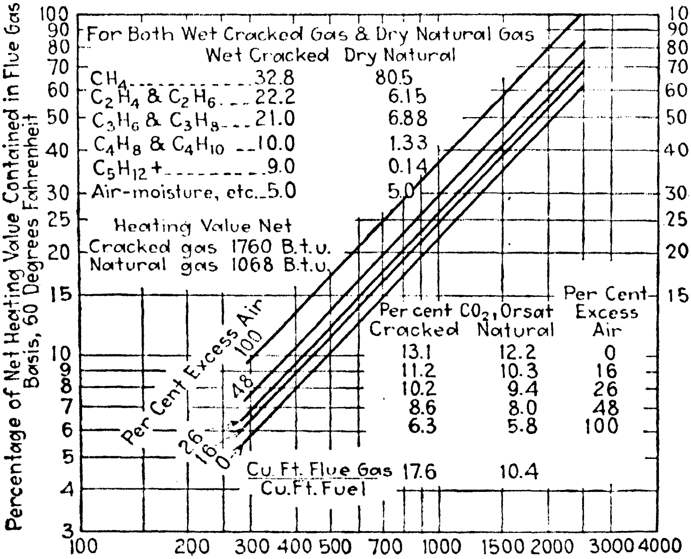

FIG. 57.—Gas combustion chart.

preferred. Steam-atomizing burners are widely used in the refinery.

In order to fire an oil fuel successfully and economically, the following factors should be considered:

1. The burners must be designed so that the oil is effectively atomized.
2. During the atomization the droplets of oil must be brought into contact with enough air (primary air) to assure continuous combustion.
3. Immediately after atomization the oil spray must be heated to cause vaporization and to promote combustion throughout the entire volume of air-fuel mixture. This is usually accomplished by the use of a fire-clay firing-tunnel through which the flame passes into the combustion space. Failure to vaporize and ignite the flame rapidly results in a long flame that tends to impinge on the heating surfaces or the furnace walls. Secondary air must be available to the flame as it leaves the firing-tunnel.
4. The furnace combustion space must be ample for a normal length of travel of the flame. The burners and heating surface must be arranged so that impingement does not take place and so that all parts of the heating surface are as nearly as possible at an equal distance from the flame. Flame impingement or local overheating is important in boilers but not so vital as in oil stills. Oils are sensitive to heat, and a condition of local overheating may cause (*a*) discoloration of the product and subsequent expensive treating operations, (*b*) a loss in viscosity of the lubricating-oil stocks, and (*c*) in extreme cases a serious decomposition with the formation of gas, lower boiling oils, and coke.

Atomizing.—The success of oil firing rests largely with the obtainment of proper atomization. The atomizing properties of an oil depend on the viscosity and to some extent on the surface tension. In general, it appears that atomization is not effective unless the viscosity of the oil is below about 30 centipoises at the temperature at which the oil is fed to the burner. This corresponds to an approximate Universal Saybolt viscosity of 150 sec. at the firing temperature. In a still more general way the proper temperature can be estimated from the gravity of the oil. The Babcock and Wilcox Company suggest

A.P.I.	11–13	14–16	15–17	17–20	20–24	24–30
Deg. F.	220–240	200–220	180–190	140–180	100–140	80–100

This tabulation should serve only for estimates, because many 10 A.P.I. cracked fuel oils do not need to be heated and some 26 A.P.I. naphthene residues must be heated to 180°F.

The amount of steam required for atomization is also dependent on the viscosity, but it is influenced more by the care used by the fireman and by the rate of firing than by the viscosity. In modern pipestill practice the steam consumption usually amounts to about 0.4 lb. of steam per pound of oil. Surveys of boiler practice indicate that the steam consumption of burners amounts to from 0.5 to 8 per cent of the total steam that is generated. This corresponds to 0.1 to 1.2 lb. of steam per pound of fuel oil. Thus an important inefficiency can exist without attracting much attention. The steam consumption for different rates of firing can be estimated from Fig. 58. These data[1] were obtained with the use of Hammel oil burners. For steam-atomizing burners the oil should be at a pressure of 40 to 60 lb. per square inch at the burner.

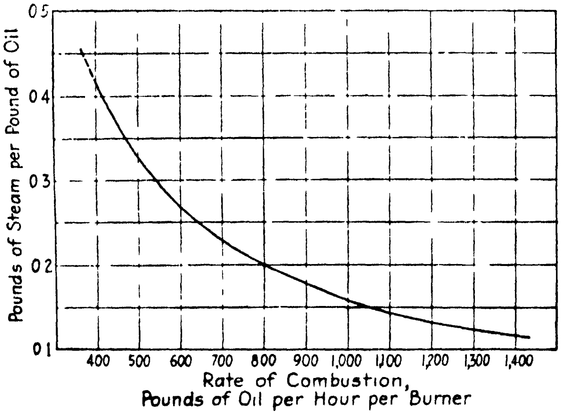

FIG. 58. Steam required to atomize oil. (*Gebhardt, "Steam Power Plant Engineering," John Wiley & Sons, New York.*)

Mechanical-atomizing burners have not been generally used in the oil industry. However, a mechanical burner or a combination steam- and mechanical-atomizing burner is useful when firing inferior fuels, such as cracked residues that contain suspended carbon or acid sludges from lubricating oil treating. These inferior fuels are supplied to the burner at 200 to 300°F. and at a pressure of 100 to 200 lb. per square inch. Acid sludge, without any treatment, can be burned in some mechanical burners, but more often the sludge is hydrolized with water and allowed to settle. Sludge may also be mixed with fuel oil and burned. The mixing is facilitated by heating to a temperature not exceeding 155°F. Gentle rolling with compressed air and recirculation by means of a pump (through filter screens) are the methods usually employed. Acid sludge is not a good fuel, but it must be disposed of, and burning is one of the simplest solutions to a troublesome problem.

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[1] GEBHARDT, G. F., "Steam Power Plant Engineering," 6th ed., p. 256, John Wiley & Sons, Inc., New York, 1928.

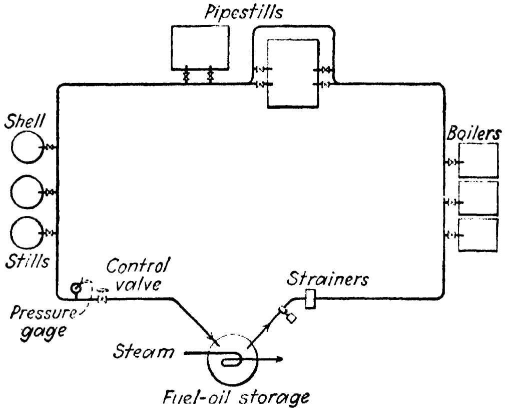

FIG. 59.—Circulating system for fuel oil.

Fuel Oil Circulating System.—The fuels that are burned in the refinery are often hardly more than waste products. Tars that are almost solid are common. Such fuels must be heated in order to pump them to the burners, and they must be circulated continuously past the burner to prevent solidification in the line. The general method of circulation is indicated in Fig. 59. In large plants the circuit may be so long that a system of parallel flow must be used. In the parallel system a small flow of oil must be maintained in each of the parallel branches.

Individual circulation systems are often maintained for each pipestill. With such an arrangement the rate of firing may be controlled by regulating the pressure in the fuel line without visiting the burner. The pressure may be conveniently regulated at a central control board. Such a system is not satisfactory unless clean, fluid fuels are available and unless minor adjustments of the firing rate are all that are necessary.

Combustion Data.—In computing an accurate heat balance as explained in Chap. XII, certain laboratory data are necessary. Among these data are (1) the heating value of fuel, (2) ultimate analysis of fuel, and (3) Orsat analysis of the flue gas. The heating value of a solid fuel may be determined by the bomb methods[2] using any of the common bombs such as the Atwater, Emerson, Parr, or Williams. The heating value of gaseous fuels is determined in Junkers-type calorimeters[3] such as the Sargent calorimeter. The ultimate analysis of fuels showing the percentage of carbon, hydrogen, etc., is determined by burning a sample of the fuel under controlled conditions and absorbing the various constituents of the combustion gas in chemical solutions. These solutions are then analyzed by the regular quantitative chemistry methods.

The Orsat-type apparatus[3] for the analysis of flue gas is offered in many modifications such as the Hay's portable analyzer, Williams', Orsat-Lunge, etc. Carbon dioxide, sulfur dioxide, oxygen, carbon monoxide, and nitrogen (by difference) can be determined in these equipments. The carbon dioxide is absorbed by a solution of caustic soda, and any other acid gases, such as sulfur dioxide and hydrogen sulfide, are absorbed with the carbon dioxide and are reported as carbon dioxide. The flue gas is cooled to room temperature during the analysis, and hence most of the water vapor that it contains is condensed. Thus the Orsat analysis is not the analysis of the gas that is present in the furnace or stack because the gas in the furnace contains water vapor. The analysis of the flue gas including the water vapor must be obtained by calculation.

Example 27. Analysis of Flue Gas from Fuel Analysis.—Fuel 1 in Table 25 is burned with 50 per cent excess air. Compute the Orsat analysis of the flue gas and the analysis of the flue gas including water vapor.
Basis: 1 lb. of Fuel 1.

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[2] Petroleum Products and Lubricants, Report of Committee D-2, A.S.T.M., 260 South Broad Street, Philadelphia, Pa.

[3] White, A. H., "Technical Gas and Fuel Analysis," McGraw-Hill Book Company, Inc., New York; Gill, A. H. "Gas and Fuel Analysis," John Wiley & Sons, Inc., New York.

$$\text{Mols C} = \frac{0.861}{12} = 0.0717$$

$$\text{Mols } H_2 = \frac{0.12}{2} = 0.0600$$

$$\text{Mols S} = \frac{0.0035}{32} = 0.0001$$

$$\text{Mols } N_2 \text{ and } O_2 = \frac{0.011}{30} = 0.0004 \text{ (assume half and half)}$$

Oxygen required (see Table 27):

$$\begin{array}{llr}
 & & \text{Mol} \\
\text{For carbon:} & 0.0717 \times 1 = & 0.0717 \\
\text{For hydrogen:} & 0.06 \times 0.5 = & 0.0300 \\
\text{For sulfur:} & 0.0001 \times 1 = & \underline{0.0001} \\
 & & 0.1018 \\
\text{Less oxygen in fuel:} & \dfrac{0.0004}{2} = & -0.0002 \\
\text{Oxygen required (no excess)} & = & \overline{0.1016} \\
\text{Excess oxygen (or air)} = 0.1016 \times 0.5 & = & \underline{0.0508} \\
\text{Oxygen required at 50 per cent excess} & = & 0.1524
\end{array}$$

Composition of air by volume is N_2 79.1 and O_2 20.9 per cent.

$$\begin{array}{llr}
\text{Nitrogen with this oxygen: } 0.1524 \times \dfrac{79.1}{20.9} & = & 0.577 \text{ mol} \\
\text{Nitrogen in fuel:} \quad \dfrac{0.0004}{2} & = & \underline{0.0002} \text{ mol} \\
\text{Nitrogen in flue gas} & = & 0.5772 \text{ mol}
\end{array}$$

ORSAT ANALYSIS

Material	Number of mols	Per cent by volume
CO_2 (and SO_2)	0.0717 and 0.0001	10.25
O_2 (excess)	0.0508	7.26
N_2	0.5772	82.49
Total		100.00

ACTUAL ANALYSIS IN FURNACE

Material	Number of mols	Per cent by volume
CO_2 (and SO_2)	0.0718	9.4
O_2	0.0508	6.7
N_2	0.5772	76.0
H_2O*	0.0600	7.9
		100.0

* Table 27.

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(For dates earlier than 1935 see First Edition)

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CHAPTER XII

HEAT AND MATERIAL BALANCES

The computation of heat, material, energy, volume, and weight balances is doubtless the most important type of computation that is available to the engineer. Practical problems always involve energy or material balances in some phase of their solution. These computations are used so generally that they are not always recognized as such.

Basis for Computation.—The selection of the basis for computation is an important factor in the ease of solution of a problem. In the solution of gas problems the most common basis is 1 cu. ft. (or 100 cu. ft.), measured at 60°F. Oil computations are usually based on the gallons of oil per hour, measured at 60°F. Fractionating-tower heat-balances are computed about the temperature datum of (1) the temperature at the vaporizer section of the tower or (2) the temperature at the top plate. Volumes of oil, A.P.I. gravities or specific gravities, and heating values are usually stated at 60°F. Analyses of oils are usually stated as percentage by volume; gas analyses are given as percentage by volume or mol per cent; and analyses of solids are given in percentage by weight.

The molecular weight is a fundamental physical and chemical unit, and computations may often be simplified by using the pound- or gram-mol as the basis. The number of computations is often cut in half by the use of the mol basis. This is particularly true if chemical reactions occur. Pound-mols of a gas (perfect) may be converted to volume, measured at 60°F., by multiplying by 379. Mols may be converted to pounds by multiplying by the molecular weight. The mol basis may be used during the calculation, and the final quantities converted from mols to pounds or cubic feet as the final step in the calculation. By Avogadro's hypothesis, equal volumes of gases contain the same number of molecules or mols. Hence the number of mols that react together is directly proportional to the volumes of gases that react, and volume percentage is proportional to mol percentage. Likewise Dalton's law of partial-pressures states that the fraction of the total pressure exerted by a gas in a gaseous mixture is proportional to its volume percentage in the mixture. Thus the following useful generalization concerning gases is possible:

Volume per cent = mol per cent = pressure per cent (partial-pressure) (13)

Many of the difficulties in the solution of problems arise because of a hazy conception of the basis upon which the computation is based. This is particularly noticeable with students, but even practicing engineers are frequently confused over the basis of a problem. In order to clarify the sequence of thought in a computation, the basis should be clearly stated at the beginning of the calculation. If it becomes convenient to adopt a new basis during the calculation, a statement of the new basis indicating its relation to the old basis should be inserted.

Conversion Constants.—In the solution of energy and material balances it becomes necessary to convert energy or mass from one form to another. The following is a list of a few of the more important conversion constants:

1 in. = 2.54 cm. = 25.4 mm.
1 ft. = 0.3048 m.
1 lb. = 0.4536 kg. (1 kg. = 2.204 lb.)
1°C. change in temperature = 1.8°F. change in temperature
Deg. Kelvin = deg. C. abs. = deg. C. + 273
Deg. Rankin = deg. F. abs. = deg. F. + 460
Deg. F. = (deg. C. + 40)1.8 − 40
Deg. C. = (deg. F. + 40) ÷ 1.8 − 40
1 standard petroleum barrel = 42 U.S. gal. (sometimes 50, lubricating-oil barrel 55)
1 bbl. per day = 1.75 gal. per hr.
1 cu. ft. = 7.48 gal.
1 gal. = 3.786 l. = 3,786 cc.
Density of water at 60°F. = 8.328 lb. per gal.
= 62.37 lb. per cu. ft.
1 atm. at sea level = 760 mm. of mercury
= 29.92 in. of mercury
= 14.697 lb. per sq. in.
= 34 ft. of water
1 lb. per sq. in. = 2.31 ft. of water
= 51.7 mm. of mercury
= 0.0703 kg. per sq. cm.

1 g.-mol volume = 22.41 l. at 0°C. and 760 mm.
1 lb.-mol volume = 359 cu. ft. at 32°F. and 760 mm.
= 379.4 cu. ft. at 60°F. and 760 mm.
1 kg.-cal. = 3.968 B.t.u.
1 cal. per g. = 1.8 B.t.u. per lb.
1 B.t.u. = 777.5 ft.-lb.
1 kw.-hr. = 1.341 hp.

Conservation of Mass.—The familiar law of the conservation of mass forms the basis for material-balance computations. This law is often stated as "The total mass of a system is the same before and after a chemical or physical change occurs." The application of this law to engineering problems is indeed simple, and often the engineer applies the law without even recognizing it. Stated in perhaps a simpler way, it may be said that all that goes into a processing system must come out of the system.

The importance of the basis that is used in a calculation is illustrated by Example 28.

Example 28. Conservation of Mass.—One thousand pounds of a solid containing 25 per cent moisture by weight is dried until it contains only 1 per cent by weight. How much water must be removed?
Basis: 1 lb. of dry solid.

Into processing system, 1.0 lb. of solid carries with it $1 \times 0.25/0.75$ or 0.333 lb. of water. One pound of solid must also leave the system.
Moisture leaving system,

$$\frac{1.0}{0.99} \times 0.01 = 0.0101 \text{ lb. of water}$$

$$\text{Water removed per lb. of dry solid} = 0.3232$$

Total water removed,

$$750 \times 0.3232 = 242 \text{ lb.}$$

Any other basis than the dry-solid basis would probably have led to undue complications, and perhaps errors might have arisen because of a befuddled conception of the basis. In many processing systems the materials entering and leaving the system are measured by volume rather than by weight, and in such cases it is always safest to convert all quantities to a weight basis.

Example 29. Gravity of Residue by Material Balance.—A 37 A.P.I. crude oil is being processed for the production of 30 per cent of 55 A.P.I. gasoline, 10 per cent of 42 A.P.I. kerosene, 15 per cent of 36 A.P.I. gas oil, and a residual stock. The percentages are by volume measured at 60°F. What is the A.P.I. of the residual stock?
Basis: 100 gal. of crude oil measured at 60°F.

Material	Per cent by volume	A.P.I.	Lb. per gal.	Lb.
Gasoline	30	55	6.316	189.5
Kerosene	10	42	6.790	67.9
Gas oil	15	36	7.034	105.3
Residue	45	?	?	?
Crude	100	37	6.993	699.3

Pounds residue stock,

$$699.3 - (189.5 + 67.9 + 105.3) = 336.6$$

Density of residue stock,

$$\frac{336.6}{45} = 7.48 \text{ lb. per gal.}$$

This corresponds to an A.P.I. of 26.

This method of solution is satisfactory because petroleum oils behave as almost pure solutions. In other words, if 1 gal. of oil A is mixed with 1 gal. of oil B, the resultant volume is 2 gal. Certain liquid combinations, such as alcohol-water and sulfuric acid-water, do not behave thus.

Conservation of Energy.—The law of conservation of energy is of more general usefulness than the law of conservation of mass. This law is also called the *first law of thermodynamics* and is stated in many different ways depending upon the use to which it is to be put. The following are perhaps the most common statements: (1) Energy in the form of heat may be converted into mechanical work, and likewise energy in the form of mechanical work may be converted into heat; (2) energy may undergo change in form but not in amount.[1] Heat and mechanical work are the most common forms of energy, and hence the law may be conveniently expressed as the following mathematical expression:

$$h = \Delta u + w \tag{14}$$

h = all energy absorbed by the system from the surroundings. Heat energy is often the only energy form that is added to the system, although any other energy addition may be included in this term.

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[1] The author suggests: The energy that goes into a system is equal to the energy that leaves the system except for changes in the internal energy content.

Δu equals the increase in the internal energy content of the system. This increase may be evidenced in any form of energy such as an increase in pressure or temperature; changes of phase such as vaporization; and increases in surface energies, chemical energy, etc. In ideal gas cycles, in which no chemical reactions occur, no change in the internal energy is possible unless the temperature changes. In such special cases the change in internal energy is equal to the energy required to heat the gas at constant volume.

w equals all work done by the system on the surroundings. Usually only the mechanical work done on the surroundings is considered, but properly this term should include all forms of energy that might leave the system, including losses.

An exceedingly useful corollary of the first law may be summarized as follows: The energy content of a system at a fixed and complete set of conditions is a constant, and hence the difference in the energy content of a system between two sets of conditions is also a constant. Because energy cannot be destroyed, it appears that the algebraic sum (or difference) of the energy inputs and expenditures required to get from one condition to another will be a constant regardless of the sequence of the changes or the number of energy changes involved.

Example 30. Heating Value at Another Temperature Than 60°F.—The heating value of methane (CH_4) is 1009 B.t.u. per cu. ft. at 60°F. What will its heating value be if the gas, along with its air, is burned at 1000°F. and the products are cooled to 1000°F.?

Basis: 1 cu. ft. of methane measured at 60°F. and 760 mm. pressure.

$$CH_4 + 2O_2 = CO_2 + 2H_2O - 1009 \text{ B.t.u. per cu. ft.}$$

Since the difference in energy content of CH_4 and O_2 at 1000°F. and the products of combustion, CO_2 and H_2O, at 1000°F. is a constant, we may complete the combustion reaction by any series of steps (Fig. 60).

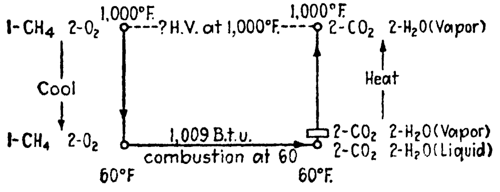

FIG. 60.—Thermodynamic cycle. Example 30.

The system is taken through the following particular series of steps because data are available for each of the operations.

Cool (sensible heat):
CH_4: $\frac{1}{379}(245 - 13,800) = -\ 35.8$ (Fig. 55)
$2O_2$: $\frac{2}{379}(200 - 7,000) = -\ 35.9$ (Fig. 55)
Gross heating value at 60°F. $1 \times (-1,009) = \underline{-1,009.0}$
$-1,080.7$

Vaporize water at 60°F. $\frac{2 \times 18}{379} \times (1,058.2) = +\ 100.4$

Heat (sensible heat):
CO_2: $\frac{1}{379}(9,850 - 245) = +\ 25.37$ (Fig. 55)
$2H_2O$: $\frac{2}{379}(8,650 - 270) = \underline{+\ 44.3}$ (Fig. 55)
Heating value of CH_4 from and to 1000°F. $= -910.63$ B.t.u. per cu. ft. (measured at 60°F.)

Example 31. Heat Required to Heat and Vaporize Gasoline.—A Mid-Continent gasoline (60 A.P.I.) at 100°F. is to be heated, vaporized, and superheated to 500°F. at atmospheric pressure. How much heat is required per pound of gasoline?

The vaporization of complex mixtures differs from the vaporization of pure compounds because vaporization occurs throughout a range of temperature. According to the corollary to the first law, the temperature at which vaporization occurs can be any temperature at which the latent heat is known, provided all of the energy changes involved are properly considered.

For comparison, the total heat input will be computed for vaporization at the temperatures of 250, 300, 350, and 400°F.

Basis: 1 lb. gasoline (Figs. 33, 34, and 37).

Vaporizing at deg. F.	Sensible heat of liquid		Latent heat		Sensible heat of vapor		Total heat, B.t.u. per lb.
250	1(250 − 100)0.563	+	131.5	+	1(500 − 250)0.53	=	348.5
300	1(300 − 100)0.58	+	124.0	+	1(500 − 300)0.541	=	348.2
350	1(350 − 100)0.595	+	116.5	+	1(500 − 350)0.554	=	348.7
400	1(400 − 100)0.61	+	110.0	+	1(500 − 400)0.568	=	349.8

This is a hypothetical situation because it would be impossible to vaporize the gasoline at different temperatures without changing the pressure, but it is an accurate and convenient method for those cases in which the exact vaporization temperature is not known (see Example 11, page 108).

Heat-balances.—Certain special cases arise in which the change in energy content of a system involves only heat energy and chemical energy, or at least other energy changes are negligible. Such processes may be studied by means of the heat-balance. With reference to the mathematical expression for the first law, all three of the items will involve changes in heat energy and chemical energy.

The following examples serve to illustrate both heat- and material balances.

Example 32. Heat-balance of a Furnace.—Fuel 12 (Table 25) is fired at 200°F. using 0.4 lb. (280°F.) of steam per pound of fuel. The flue gas has an Orsat analysis of 13.0 per cent CO_2, 4.25 per cent O_2, and 82.75 per cent N_2. The heat gainfully used to heat oil amounts to 1,367,000 B.t.u. The stack temperature is 800°F. The air is at 80°F. and has a relative humidity of 50 per cent. The vapor-pressure of water at 80°F. is 26.6 mm. The still is operating in a continuous manner.

Basis: 100 lb. of oil 12, 60°F. temperature datum.

The ultimate constituents in the fuel undergo the following chemical reactions:

$$\begin{array}{ll} C + O_2 & = CO_2 \\ H_2 + \frac{1}{2}O_2 & = H_2O \\ S + O_2 & = SO_2 \\ H_2O \text{ (liquid)} & = H_2O \text{ (vapor)} \end{array}$$

Mols of combustion products:

Carbon............. $\frac{87.6}{12} = 7.3$

Sulfur............. $\frac{0.7}{32} = 0.02$ (reported as CO_2 by Orsat)

Hydrogen........... $\frac{10.27}{2} = 5.14$

Water.............. $\frac{0.05}{18} = 0.003$ (neglect)

Undetermined....... $\frac{1.38}{30} = 0.05$ (considered as O_2 and N_2, equal parts)

Material balance of carbon:

Mols of dry flue gas from 100 lb. of fuel. Mol per cent = volume per cent (gases).

All of the carbon is found in the carbon dioxide (13 per cent).

$$\begin{array}{ll} \text{Mols } CO_2 \text{ (and } SO_2) & = 7.32 \\ \text{Mols } N_2 = 7.32 \times \frac{82.75}{13} & = 46.50 \\ \text{Mols } O_2 = 7.32 \times \frac{4.25}{13} & = 2.39 \\ \text{Total mols of dry flue gas} & = \overline{56.21} \text{ mols} \end{array}$$

Material balance of oxygen:

Air required:

$$\text{Mols } N_2 \text{ from air} = 46.5 - \frac{0.05}{2} = 46.475$$

$$\text{Mols } O_2 \text{ used} = 46.475 \times \frac{20.9}{79.1} + .025 = 12.28$$

$$\text{Mols air} = 46.475 \times \frac{1}{0.791} = 58.7$$

Percentage of excess air:

$$O_2 \text{ required for C and S} = 7.32 \text{ mols}$$

$$O_2 \text{ for hydrogen} = \frac{5.14}{2} = 2.57$$

$$O_2 \text{ required} = 9.89 \text{ mols}$$

$$\text{Percentage of excess } O_2 \text{ or air} = \frac{12.28 - 9.89}{9.89} \times 100 = 24.2 \text{ per cent}$$

Material balance of water vapor:

Water in	Mols
Atomizing steam $= 100 \times \frac{0.4}{18}$	= 2.22
From H_2 in fuel (same number mols as H_2)	= 5.14
From air $= \frac{13.3}{(760 - 13.3)}\, 58.7$	= 1.04
Free moisture in fuel (negligible)	= 0.00
Total	= 8.40

The water vapor leaving the system in the flue gas must equal the water coming into the system, or 8.4 mols.

Heat balance:

Heat Entering System		B.t.u.
Net heating value of fuel	17,479 × 100 =	1,747,900
Heat in air (note Fig. 55)	58.7(336 − 196) =	8,210
Heat in steam (see Fig. 55 or steam tables)	0.4 × 100(2,200 − 260) ÷ 18 =	4,310
Sensible heat content of fuel oil	100(200 − 60)0.442 =	6,190
		1,766,610

All of this heat will be recovered from the system if the flue gas is cooled to 60°F.

Heat Leaving System		
Sensible heat content (see Fig. 55) at 800°F.		
CO_2	7.32(7,600 − 245) =	53,900
Water vapor	8.4 (6,800 − 260) =	54,900
Diatomic gases (N_2 and excess O_2)	48.89(5,500 − 200) =	259,000
		367,800 B.t.u.

Summary of heat-balance:

Heat	B.t.u.	Per cent
Into system	1,766,610	100.0
Out of system:		
Useful heat (given)	1,367,000	77.35
Stack loss	367,800	20.85
Unaccounted for and losses	31,810	1.8
	1,766,610	100.0

Approximate stack loss using Fig. 56:
Stack loss at 800°F. and with 13 per cent CO_2 in the flue gas (25 per cent excess air) = 19.6 per cent (in foregoing, 20.85 per cent)

In this example the system consists of the fuel, air, steam, and the products of combustion. The products include the combustion gas, excess air, atomizing steam, and the water vapor from the air.

Applying the equation

$$h = \Delta u + w$$

the symbol h refers to the sensible heat content of the air above 60°F., the sensible heat content of the steam above 60°F., and the sensible heat content of the fuel above 60°F.

The change in internal energy (Δu) is represented by the decrease in chemical energy as the fuel burns. The system decreases in energy content by the amount of the net heating value of the fuel. In combustion calculations the heat input is considered as ($h + \Delta u$), which amounts algebraically to transferring the Δu term in the foregoing equation as follows:

$$h - (-\Delta u) = w = h + \Delta u$$

The work done or the heat added to the surroundings is represented by w. This term consists of the stack losses (eventually transferred from the system to surroundings); the heat lost to the furnace walls, air, soil, foundations etc.; and the useful heat.

Example 33. Heat-balance of a Fractionating Tower.—The simple tower system shown in Fig. 61 will be studied by means of a heat-balance to determine the amount of reflux (286°F.) that must be supplied in order to cause the tower to function as a fractionating device. Capacity, 1,200 bbl. per day.
Basis: 1 hr., 2,100 gal. per hr.

The properties of the feed and products are as follows:

	Volume, per cent	A.P.I.	Lb. per gal.	Gal. per hr.	Lb. per hr.	50 per cent B.P.	Mol. wt.	Latent heat
Gasoline	26.8	62.8	6.06	563	3,415	260	119	126
Naphtha	5.63	52.8	6.39	118	754	370	156	110
Kerosene	19.8	45.6	6.65	416	2,765	460	195	100
Gas oil	10.6	39.4	6.89	222	1,530	585	272	84
Reduced crude	36.97	31.2	7.24	776	5,610			
Loss	0.2	....	....	.....	96			
Crude	100.00	43.0	6.75	2,100	14,170			

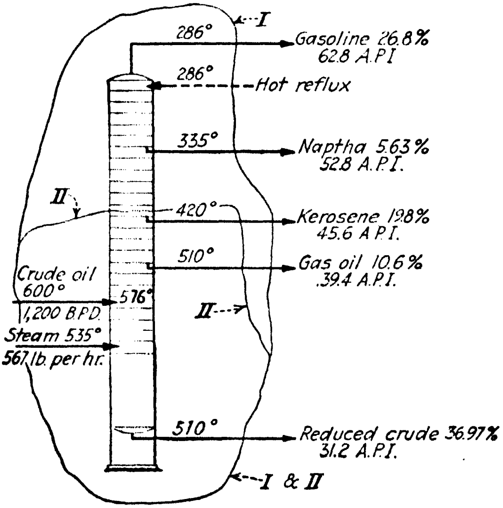

FIG. 61.—Simple tower system. Example 33.

This problem might be analyzed as the preceding example, by using a temperature basis of 60°F. However, the solution is facilitated by selecting the vaporizer temperature as the temperature datum and computing directly the heat that must be removed from the system by the reflux.

Basis: Temperature datum 576°F.

The system consists of the crude oil and process steam. At 576°F. the gasoline, naphtha, kerosene, and gas oil are vapors and the reduced crude oil is a liquid. A sufficient quantity of heat must be removed from the vapors to cool them to the temperatures at which they are withdrawn from the tower and to condense the naphtha, kerosene, and gas oil at their withdrawal temperatures.

Heat to be removed by the reflux:

Sensible heat:

		B.t.u.
Gasoline	3,415(576 − 286)0.56 × 1.06 =	589,000
Naphtha	754(576 − 335)0.565 × 1.06 =	108,900
Kerosene	2,765(576 − 420)0.58 × 1.06 =	265,000
Gas oil	1,530(576 − 510)0.592 × 1.06 =	63,500
Reduced crude	5,610(576 − 510)0.722 × 1.03 =	276,000
		1,302,400
Steam	567(535 − 286)0.5 =	70,600
		1,373,000
Latent heat:		
Naphtha	754 × 110 =	82,800
Kerosene	2,765 × 100 =	276,500
Gas oil	1,530 × 84 =	128,500
Total heat to be removed	=	1,860,800

The gasoline, naphtha, kerosene, and gas oil were cooled as vapors, and hence the specific heats of vapors (Fig. 34) were used, but the reduced crude oil was cooled as a liquid (Fig. 33).

Bernoulli's Theorem.—Bernoulli's theorem is used in the solution of many hydraulics problems. This theorem is a special case of the first law of thermodynamics in which changes in the energy content of a fluid system are balanced against one another. Although friction losses are evident as heat, the theorem is concerned only with the pressure and energy changes, and heat is considered lost energy. Bernoulli's theorem may be stated as follows:

$$\left.\begin{array}{r} X_a \text{ (static head)} \\ +\dfrac{u_a^2}{2g} \text{ (velocity head)} \\ +P_aV_a \text{ (pressure head)} \\ +W \text{ (mechanical work)} \end{array}\right\} = \left\{\begin{array}{l} X_b \\ +\dfrac{u_b^2}{2g} \\ +P_bV_b \\ +F \text{ (friction)} \end{array}\right\} \tag{15}$$

Example 34. Hydraulic Energy Balance.—A tank of water at 150°F. (specific gravity 0.985, viscosity 0.433 centipoise) is discharging through a standard 2-in. pipe system at the rate of 120 gal. per min. by its own hydrostatic head. Figure 62 indicates the pipe system. What is the height of the water above the discharge point?

In this problem the only energy input to the system is the difference in the static head ($X_a - X_b$). This energy is dissipated as friction losses in the pipe and fittings, in the entrance to the line from the tank, and as kinetic energy in the fluid as it flows from the end of the pipe.

Basis: 1 sec., isothermal at 150°F.

$$\text{Velocity} = \frac{120 \times 144}{7.48(1.035)^2 \times 60 \times 3.1416} = 11.5 \text{ ft. per sec.}$$

$$\text{Velocity head} = \frac{u_b^2}{2g} = \frac{(11.5)^2}{2 \times 32.2} = 2.05 \text{ ft. of fluid}$$

Friction losses (see Fig. 54):

$$\text{Contraction loss at connection to tank} = \frac{ku_b^2}{2g} = 0.5 \times 2.05 = 1.025 \text{ ft. of fluid}$$

Loss in pipe and fittings (see Fig. 53):

$$\text{Equivalent length of pipe} = 60 + 15 + \frac{2.07}{12} \times 45 + \frac{5 \times 2.07 \times 30}{12}$$

$$= 108.66 \text{ ft.}$$

$$\Delta P_f = \frac{0.323 fsu^2L}{D} \qquad \frac{Dus}{z} = \frac{2.07 \times 11.5 \times 0.985}{0.433} = 54.1$$

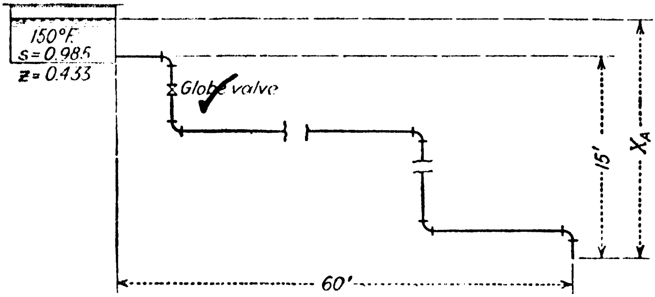

Fig. 62.—Simple hydraulic system. Refer to Example 34.

Friction factor for new, clean pipe = 0.0046

$$\Delta P_f = \frac{0.323 \times 0.0046 \times 0.985(11.5)^2 108.66}{2.07}$$

$$= 10.1 \text{ lb. per sq. in.}$$

$$= \frac{10.1 \times 144}{62.4 \times 0.985} = 23.8 \text{ ft. of fluid}$$

Difference in head required $= X_a - X_b = 2.05 + 1.025 + 23.8 = 26.9$ ft.

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CHAPTER XIII

HEAT TRANSFER

The solution of problems that involve the transfer of heat is difficult because of the lack of adequate data. The film transfer rates can be computed with reasonable accuracy for clean or new pipe, but the effect that dirty or corroded pipe surfaces will have on the transfer rate cannot be satisfactorily estimated. With the greatest possible care, the accuracy with which the rate of heat transfer can be computed is probably not better than ±10 per cent. Nevertheless, even this accuracy cannot be attained unless the designer thoroughly understands the fundamentals of heat transfer.

The dismaying lack of data on the effect of the surface condition has caused many engineers to turn to the use of over-all coefficients of heat transfer. Although the use of the over-all coefficient is convenient and sometimes necessary, most heat-exchange experts feel that the use of over-all coefficients is inaccurate and that an attempt to compute or estimate the individual film coefficients is always the safest method to use. In this chapter the film transfer coefficients for materials contained in clean or new equipment will be studied, and in Chap. XXI transfer rates for commercial equipments will be discussed.

There are three common methods of transferring heat, *viz.*, radiation, conduction through solids, and conduction through fluids. In practice a combination of two or even all of these methods may take place simultaneously.

Radiation.—Although radiation is probably the most important method of transferring heat, the calculation of the rate at which radiation occurs in many commercial furnaces is impossible. In Chap. XXII are examples of radiation calculations for the particular case of the tubestill heater.

Nevertheless, qualitative study of radiation theory leads to a clearer insight into this method of transferring heat. The transfer of heat by radiation is governed by Stefan's law:

$$Q = bAT^4$$

where A = area of radiating surface, sq. ft.
T = absolute temperature of the surface, deg. F.
Q = B.t.u. transferred per hr.
b = 1.72×10^{-9} B.t.u./(deg. F. diff.)(sq. ft.)(hr.) at black-body conditions.

But a surface cannot radiate all of this heat to another surface because the cooler surface also radiates heat. For a small body completely surrounded by a hotter body the foregoing statement simplifies to

$$Q = \text{net heat transferred} = Q_2 - Q_1 = bA(T_2^4 - T_1^4) \quad (16)$$

This expression involves the assumption that all of the energy emitted by the hot body is absorbed by the cooler body and that all of the energy emitted from the cooler body is absorbed by the hotter body. In practice most materials fail to absorb all of the radiant energy that falls upon them, and hence the constant b is different for all materials.

Materials that have a rough or dull-finish surface absorb radiation almost as completely as perfect radiation absorbers (black bodies), but polished surfaces or even clean metallic rough surfaces reflect a large part of the radiation that falls upon them and hence require a corrected value of b. Furthermore, it appears that surfaces such as a brick wall at incandescent temperatures reflect much of the radiation that falls upon them. Table 28 gives common values of b.

TABLE 28.—RADIATION CONSTANTS

Material	$b \times 10^{-9}$
1. Perfect black body	1.72
2. Brass, matte	0.374
3. Cast iron, rough and highly oxidized	1.57
4. Clay	0.65
5. Copper	0.278
6. Ceramics ware, unglazed	1.34
7. Field soil	0.63
8. Granite, smooth but not polished	0.745
9. Lamp black	1.56
10. Lime mortar, rough	1.51
11. Sheet iron, matte oxidized	1.55
12. Sheet iron, polished	0.466

The differences in the fourth powers of the temperature are involved in this formulation, and it becomes apparent that the higher temperature raised to the fourth power may be so large that the lower temperature may be neglected. Furthermore, the quantity of heat that is radiated increases very rapidly for small increases in temperature. The following tabulation indicates the rate of increase:

$1{,}000^4 = 1 \times 10^{12}$
$1{,}200^4 = 2.1 \times 10^{12}$
$1{,}400^4 = 3.9 \times 10^{12}$
$1{,}600^4 = 6.6 \times 10^{12}$
$1{,}800^4 = 10.5 \times 10^{12}$
$2{,}000^4 = 16.0 \times 10^{12}$

Thus the temperature was doubled but the radiation increased sixteenfold.

Another deduction of a qualitative nature but of great value regards the angle of vision or sight of a point radiation source. Radiation is a wave phenomenon, and it travels through gaseous materials in a straight line without suffering much of a loss in intensity. It is unable to penetrate opaque or dark solid materials. Thus cooling surfaces cast what might be called radiation shadows behind them, and the space shielded from radiation is not heated by radiation.

In most combustion problems the radiation of heat is practiced by allowing combustion to take place in proximity to cooled surfaces. Radiation from flames and gases cannot be easily handled by Eq. (16) because (1) the size of the flame cannot be accurately determined, (2) the flame has a thickness so that radiation from the center of the flame must penetrate the outer layers, and (3) the luminosity of flames varies with different fuels and conditions of combustion. In nonluminous flames, radiation is found to be dependent to a large extent on the percentage of carbon dioxide and water vapor that is present. However, radiation from such a flame is not effective, and the presence of partially burned carbon particles (luminous flames) greatly increases radiation. The problem of radiation from flames is further complicated by the convection heat transfer that occurs by the circulation of gases within the furnace box.

CONDUCTION THROUGH SOLIDS

Conduction is the most simple method of heat transfer. Newton's fundamental law of resistances and driving forces, if applied to conduction, takes the following form:

$$Q = \frac{kA(T_2 - T_1)}{L} \tag{17}$$

where Q = B.t.u. heat transferred per hr.
A = area of surface, sq. ft.
T_2 and T_1 = temperatures at hot and cold surfaces.
k = conductivity as B.t.u./(deg. F. diff.)(sq. ft.)(hr.) for 1 ft. thickness.
L = thickness, ft.

The values of k for some common materials are given in Table 29.

TABLE 29.—THERMAL CONDUCTIVITY
Conductivity: B.t.u./(deg. F. diff.)(sq. ft.)(hr.) for 1 ft. thickness

Material	70°F.	212°F.	500°F.	1800°F.
Brass (70–30)	63	72.5		
Copper	227	220.0		
Iron (wrought)	35	35.0		
Iron (cast)	22–36			
Steel (0.1 per cent carbon)	26.1	25.8	25.0	
Alloy steel, austenitic chrome-nickel	......	......	10.4	
Calcium carbonate (scale)	0.5–1.5			
Porcelain	0.6			
Magnesia (85 per cent)	......	0.04		
Asbestos (felt)	......	0.12		
Cork	......	0.03		
Portland cement	0.5			
Brick or mortar wall	0.4			
Concrete wall	......	......	0.505	0.70
Red brick	0.39	0.43	0.52	0.95
Firebrick and clay-bond silica	0.48	0.5	0.56	0.82
Sil-o-cel brick	0.125	......	......	0.125
Carborundum brick	......	......	5.6	6.4
Magnesite brick	......	......	3.5	2.3
Silica brick	......	......	0.7	1.15
Asbestos cement board (transite)	......	0.23	......	0.23

Table 30 presents the conductivities of petroleum oils.[1]

TABLE 30.—THERMAL CONDUCTIVITY OF PETROLEUM PRODUCTS AND WATER
B.t.u./(deg. F. diff.)(hr.)(sq. ft.) for 1 ft. thickness

Temperature, deg. F.	A.P.I. at 60°F.	Water	10	20	30	40	50	60	Asphalt	Wax
	Sp. Gr. 60/60		1.0	0.934	0.8762	0.8521	0.7796	0.7389		
0		0.322*	0.0683	0.0735	0.0783	0.0833	0.0875	0.0925	0.1	0.133
200		0.41	0.0642	0.0691	0.0735	0.0783	0.0825	0.0875	(Average from 32°F. to melting-point)	
400		......	0.06	0.0642	0.0691	0.0735	0.0775	0.0815		
600		......	0.0558	0.06	0.0642	0.0683	......	......		
800		......	0.0525	0.0558	0.0591	......	......	......		

* At 35°F., also 0.357 at 100°F.

In using Newton's law, the factor L/kA may be considered to be a resistance (R) to the driving force represented by the temperature difference ($T_2 - T_1$). The equation may be rearranged as

$$Q = \frac{\Delta T}{L/kA} = \frac{\Delta T}{R} \tag{18}$$

When heat is transferred by conduction, several materials usually compose the vessel or wall through which heat is being conducted, and hence conduction problems involve the conduction of heat through a series of resistances. The quantity of heat Q that passes through each material is the same, but the temperature difference across each material will be different for each material. Suppose a flat wall is composed of three materials having conductivities of k_1, k_2, and k_3, having thicknesses of L_1, L_2, and L_3, and having temperature differences of ΔT_1, ΔT_2, and ΔT_3. The heat that is conducted per square foot per hour is

$$Q = Q_1 = Q_2 = Q_3 \quad \text{and} \quad \frac{\Delta T_1}{L_1/k_1A_1} = \frac{\Delta T_2}{L_2/k_2A_2} = \frac{\Delta T_3}{L_3/k_3A_3}$$

Also

$$\Delta T_1 = Q\frac{L_1}{k_1A_1}, \qquad \Delta T_2 = Q\frac{L_2}{k_2A_2}, \qquad \Delta T_3 = Q\frac{L_3}{k_3A_3}$$

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[1] CRAGOE, C. S., *Misc. Pub. Nat. Bur. Standards* 97, 1929.

The temperature difference across the three materials is the sum of the three individual differences, and hence the following relation may be written:

$$Q\left(\frac{L_1}{k_1A_1}+\frac{L_2}{k_2A_2}+\frac{L_3}{k_3A_3}\right)=\Delta T_1+\Delta T_2+\Delta T_3=\Delta T$$

and

$$Q=\frac{\Delta T}{\dfrac{L_1}{k_1A_1}+\dfrac{L_2}{k_2A_2}+\dfrac{L_3}{k_3A_3}}=\frac{\Delta T}{R_1+R_2+R_3} \tag{19}$$

Thus we find that the resistance to the flow of heat corresponds exactly to the resistance to the flow of electricity through a series electrical circuit. The temperature differences are directly proportional to the resistances to flow, so that

$$\Delta T:\Delta T_1:\Delta T_2:\Delta T_3::R:R_1:R_2:R_3 \tag{20}$$

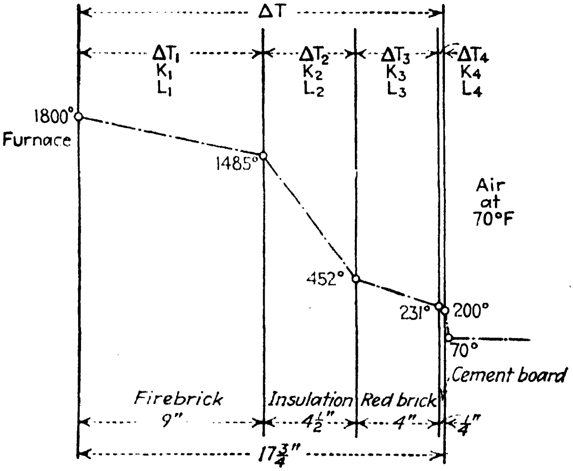


FIG. 63.—Temperature inside of a furnace wall. Refer to Example 35.

Example 35. Heat Loss through a Furnace Wall.—A furnace wall consists of 9 in. of firebrick, 4½ in. of sil-o-cel brick, 4 in. of red brick, and ¼ in. of transite board. The conductivity coefficients for these materials are given in Table 29. The inside wall of the furnace is at 1800°F., and let us assume that the outside of the wall is at 200°F.*

---

* Since the outside temperature cannot be easily measured, the air temperature is usually used, but this involves the conductivity of a film of stagnant air at the wall (see Example 38, p. 214).

How much heat is lost per hour through a surface of 10 sq. ft.? (See Fig. 63.)
Basis: 1 sq. ft.

The surface is the same through each of the materials, and hence the area has been left out of all of the formulations [see Eq. (19)].

$$Q = \frac{\Delta T}{\frac{L_1}{k_1} + \frac{L_2}{k_2} \cdots} = \frac{1800 - 200}{\frac{9}{12 \times 0.82} + \frac{4.5}{12 \times 0.125} + \frac{4}{12 \times 0.52} + \frac{0.25}{12 \times 0.23}}$$

$$= \frac{1600}{0.915 + 3.0 + 0.641 + 0.0905} = \frac{1600}{4.646}$$

= 344 B.t.u. per sq. ft.

= 3440 B.t.u. through the 10 sq. ft.

The temperatures within the wall can be computed by Eq. (20).

$$\frac{\Delta T}{\Delta T_1} = \frac{R}{R_1}$$

Location	Temperature difference	Temperature deg. F.
Between firebrick and sil-o-cel	$\frac{1600}{4.646} = \frac{\Delta T_1}{0.915}$ $\Delta T_1 = 315$	1485
Between sil-o-cel and red brick	$\Delta T_2 = 1033$	452
Between red brick and transite	$\Delta T_3 = 221$	231
At outer wall (as a check)	$\Delta T_4 = 31$	200

Pipe Insulation.—In the case of pipe insulation the area through which heat is transferred is not constant. If the thickness of the material is small, compared with the diameter, the arithmetic average of the larger area and the smaller area may be used. The arithmetic mean area may be used for all cylindrical vessels and for pipe sizes down to about 2 in. if standard insulation is used and if an error of 4 per cent is permitted. If the thickness is great compared with the diameter, the logarithmic mean area must be used:

$$\text{Logarithmic area} = \frac{A_2\ (\text{large}) - A_1\ (\text{small})}{2.3 \log \frac{A_2\ (\text{large})}{A_1\ (\text{small})}} \qquad (21)$$

Table 31 shows the error if the arithmetic area is used instead of the logarithmic area.

TABLE 31

Pipe size, in.	Standard insulation			High-temperature insulation*		
	Thickness, in.	log mean area†	Approx. error, per cent	Thickness, in.	log mean area†	Approx. error, per cent
½	⅞	4.9	10	1½	6.2	19.0
1	⅞	6.53	5	1½	7.95	11.5
1½	⅞	8.41	4	1½	9.9	7.5
2	1 1/32	10.4	4	1½	11.5	5.8
3	1 1/32	14.0	2	2½	17.65	6.3
4	1⅛	17.4	1½	2½	21.1	4.0
5	1⅛	20.8	1	2½	24.5	3.5
6	1⅛	.....	....	2½	28.0	2.0
8	1¼	.....	....	2½	34.6	1.0
12	1½	44.8	....	3	49.6	

* High-pressure steam lines, oil lines above about 400°F., etc.

† Square inches per inch of length.

CONDUCTION THROUGH FLUID FILMS

The heating of fluids through the walls of a metal container is at the same time an important and a most troublesome method of transferring heat. As indicated in Chap. X all fluids are bounded at the retaining walls by a film of stagnant fluid. Heat must be transferred through these films by conduction. The films are very thin, their thicknesses cannot be easily measured, and hence the thickness L which is involved in the resistance of the film cannot be determined directly. In order to avoid this difficulty, the resistances of fluid films have been correlated by expressing the resistance as $1/h$ in which h is the film coefficient of heat transfer. From commonly accepted heat-transfer coefficients the apparent film thickness varies from about 0.1 for gases to about 0.0001 in. for condensing steam. If the conduction equation is applied to the transfer of heat from a fluid into a solid partition wall and into another fluid, the conduction equation takes the following form:

$$Q = \frac{\Delta T}{\dfrac{1}{h_1 A_1} + \dfrac{L_2}{k_2 A_2} + \dfrac{1}{h_3 A_3} + R_D} \qquad (22)$$

In this equation h_1 and h_3 represent the film coefficients of heat transfer for the two fluids; L_2 and k_2 are the thickness and conductivity of the partition wall; and R_D is the resistance due to corrosion, dirt, or roughness of the surfaces. The resistances indicated in the denominator may, for convenience, be added, and the total equals $1/H$ in which H is the over-all rate of heat transfer. Returning to the first equation of conduction, we see that it may be stated as follows:

$$Q = \frac{A\Delta T}{1/H} = HA\Delta T \tag{23}$$

Thus if an average area is used,

$$\frac{1}{H} = \frac{1}{h_1} + \frac{L_2}{k_2} + \frac{1}{h_3} + R_D$$

$$H = \frac{1}{\frac{1}{h_1} + \frac{L_2}{k_2} + \frac{1}{h_3} + R_D} \tag{24}$$

If one of the film coefficients is small compared with the other coefficients, the resistance $1/h$ which corresponds to it will be proportionally large. In such a case the value of the over-all coefficient will be nearly the same as the small film coefficient. For the same reason the resistance of the metal wall may often be neglected.

Example 36. The Over-all Coefficient of Heat Transfer.—Heat is being transferred from a gas through the walls of a standard 2-in. pipe and into water that is flowing on the inside of the pipe. $h_G = 6$, $h_W = 500$, and k for the pipe wall is 25 [see Eq. (24)].

$$H = \frac{1}{\frac{1}{h_G} + \frac{L}{k} + \frac{1}{h_W}} = \frac{1}{\frac{1}{6} + \frac{0.154}{12 \times 25} + \frac{1}{500}}$$

$$H = \frac{1}{0.1667 + 0.00051 + 0.002} = 5.91$$

Thus the resistance of the metal wall and the water film could be neglected with an error of only 1.52 per cent.

Likewise, the pipe could be made of copper, which is an excellent conductor of heat ($k = 220$), and the over-all coefficient would be changed by only a small amount.

$$H = \frac{1}{0.1667 + 0.000058 + 0.002} = 5.93$$

Factors That Affect the Film Coefficient.—Exactly as in conduction through solids, a temperature difference exists across fluid films. The temperature difference in the film causes convection currents that tend to decrease the thickness of the film, and forced circulation of the fluid past the heating surface has the same effect. Thus the numerical value of the film coefficient is directly dependent on the thickness of the film and the material that composes the film.

Some of the factors that affect the thickness of the film are:

1. Viscosity.
2. Density.
3. Velocity in main body of fluid.
4. Conductivity.
5. Shape of retaining walls and turbulence caused by such disturbances as bends.
6. Specific heat.
7. Latent heat, in the case of vaporization or condensation.
8. Materials or impurities having low conductivities, that may accumulate in the film and retard mixing. Examples of this are (*a*) air in steam, (*b*) paraffin wax in oils, and (*c*) materials that may corrode the metal surface.
9. Temperature.

Temperature is not in itself important, but it does affect the value of the other physical constants. For example, the viscosity changes rapidly with temperature, and hence temperature becomes indirectly of great importance. An examination of these factors indicates why some coefficients are low and others are high. The coefficients for lubricating oils are low mainly because the viscosity is high; the coefficients for gasoline and water are high because of the high fluidity of these materials. However, the conductivity of water is much higher than the conductivity of oils, and hence the coefficients for water are even higher than for gasoline. Similarly the viscosity of gases is low, but the conductivity is extremely low, so that the coefficients for gases are low. Finally, paraffin-containing stocks when cooled to fluid-body temperatures of even 300°F. may deposit a thin but effective film of solid paraffin wax so that heat transfer is greatly retarded.

Film Temperature.—Obviously the several physical properties mentioned above should be taken at the mean temperature of the film. However, the effect of temperature on the value of these constants, except the viscosity, is not great. The arithmetic mean film temperature is usually considered as sufficiently accurate. Although the use of the film temperature is most exact, the computation of film temperatures is tedious, and hence many of the formulae for transfer rates, as given in the following pages, are based on viscosities measured at the temperature of the main body of fluid. The film temperature may be computed by noting that the film resistances are directly proportional to the temperature drop across the film. If the area is the same at each film, the film temperature may be expressed in terms of the total temperature difference and the film coefficients as follows:

$$\Delta T:\Delta T_1:\Delta T_2:\Delta T_3:, \text{ etc.}: : \frac{1}{H}:\frac{1}{h_1}:R_D:\frac{1}{h_3}:, \text{ etc.}$$

$$\frac{\Delta T_1}{\Delta T} = \frac{1/h_1}{\dfrac{1}{H}} = \frac{1/h_1}{\dfrac{1}{h_1} + R_D + \dfrac{1}{h_3}}$$

$$\Delta T_1 = \frac{\Delta T \dfrac{1}{h_1}}{\dfrac{1}{h_1} + R_D + \dfrac{1}{h_3}} = \Delta T\left(\frac{h_3}{h_3 + h_1 h_3 R_D + h_1}\right)$$

Let

$\Delta T_1 = T_1 - T_2$; $\Delta T_2 = T_2 - T_3$; etc. and $\Delta T = T_1 - T_4$

where T_1 = high temperature.

T_4 = low temperature.

Film temperature in film 1 or hot film $= T_1 - \dfrac{\Delta T_1}{2} =$

$$T_1 - \frac{\Delta T}{2}\,\frac{h_3}{h_3 + h_1 h_3 R_D + h_1} \tag{25}$$

Film temperature in film 2 or cold film =

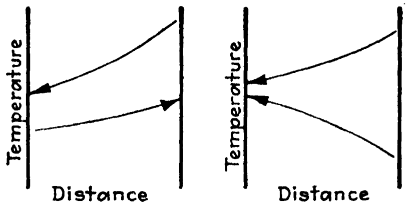
$$T_4 + \frac{\Delta T}{2}\,\frac{h_1}{h_3 + h_1 h_3 R_D + h_1} \tag{26}$$

For the simple case where $h_1 = h_3$, and R_D is negligible

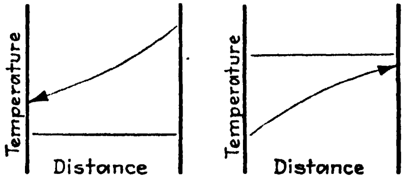
$$\text{Hot-film temperature} = T_1 - \frac{\Delta T}{4}$$

$$\text{Cold-film temperature} = T_4 + \frac{\Delta T}{4}$$

The Temperature Difference.—In the case of conduction through solids the temperature difference ΔT is usually the same at all points, but in the case of fluid systems the temperature difference is not the same at all points because as one fluid is heated, the other is cooled. In Fig. 64 the arrows indicate the direction of flow of the fluids with respect to one another for the common arrangements of flow. Almost all commercial equipments are designed for countercurrent flow or at least for conditions that approach countercurrent flow. The conditions indicated in *c* and *d* (Fig. 64) are closely simulated in steam heaters and in coil-in-box coolers.



(a) Countercurrent (b) Parallel



(c) Constant Cooling Temperature (d) Constant Heating Temperature

FIG. 64.—Common arrangements of flow.

The temperature difference for a fluid system is an average quantity. For the simplified case of a constant transfer coefficient and constant specific heats for the two fluids, the logarithmic mean temperature difference is valid:

θ = log mean temp. diff. =

$$\frac{\text{larger temp. diff.} - \text{smaller temp. diff.}}{\log_e \dfrac{\text{larger temp. diff.}}{\text{smaller temp. diff.}}} \qquad (27)$$

The logarithm to the base 10 may be converted to base *e* by multiplying by 2.3.

Example 37. The Logarithmic Mean Temperature Difference.—An oil is to be cooled from 200 to 100°F. by water that enters at 60 and leaves at 80°F. [see Eq. (27)].

$$\theta = \frac{(200 - 80) - (100 - 60)}{\log_e \frac{120}{40}} = \frac{80}{1.1} = 72.8°\text{F.}$$

The arithmetic temperature difference would be in error by about 10 per cent.

$$\text{Arithmetic } \Delta T = \frac{120 + 40}{2} = 80°\text{F}.$$

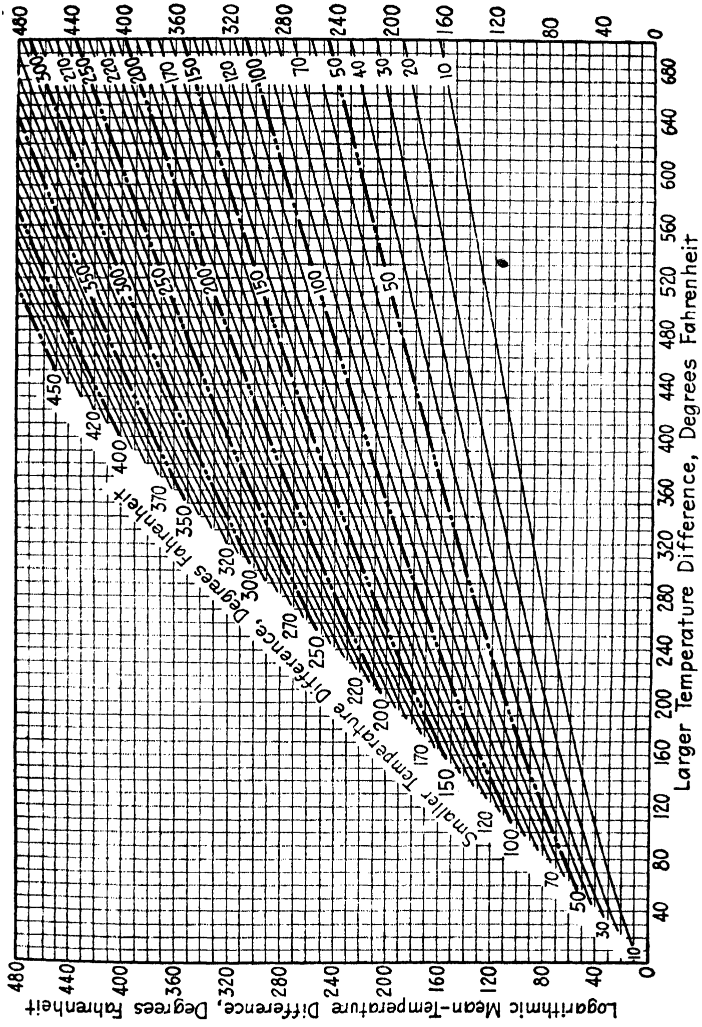


FIG. 65.—Logarithmic mean temperature difference.

If the ratio of the temperature differences is less than 2, the arithmetic average temperature difference may be used with an error of only 4 per cent. For convenience the logarithmic temperature differences are plotted in Fig. 65 as a function of the larger and smaller temperature differences.

The logarithmic temperature difference is accurate enough for materials such as air, water, and steam, whose viscosity does not change rapidly with temperature, but in the case of lubricating oils it may be far in error. Suffice here to say that the logarithmic temperature difference may cause errors as high as 20 per cent when exchanging heat between two viscous petroleum oils.

NUMERICAL VALUE OF FILM COEFFICIENTS

The following formulations have been presented for the computation of film coefficients when the heating surfaces are clean. After even a few days of service the transfer rates may drop to values much lower than these equations indicate. For information concerning other fluids or conditions, refer to "Heat Transmission" by McAdams[2] or to textbooks on chemical engineering.

Gases—Natural-convection and Radiation Combined.—Convection is always accompanied by radiation, and hence the most convenient method of computing heat losses from an exposed surface to air is by a coefficient that represents both the convection and radiation transfer of heat. A study of the literature on this subject shows that the coefficient is substantially the same for vertical brick, asbestos, metal, canvas, and wood surfaces. The following formula was obtained by using data for all of these materials between temperatures of 100 and 500°F. when the materials are in a vertical position.

$$h_G = 1.5 + 0.0058(\Delta t)_f \qquad (28)$$

When the surface is horizontal, the rate h_G is about 25 per cent higher for the upper surface than the values given by Eq. (28) and about 15 per cent lower for the under surface. Note that Δt is the temperature difference across the air film.

Example 38. Natural-convection Film.—In Example 35 (page 206) the temperature of the wall was assumed to be 200°F. This temperature is

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[2] "Heat Transmission," McGraw-Hill Book Company, Inc., New York, 1933.

The film rates are much higher than those obtained in commercial equipment because the experimental equipment was carefully cleaned after each run. Difficulty is encountered in determining the average mass velocity through the tube bundle and baffles. McAdams[2] also presents some information.

Condensing-vapor Film.—The films formed during the condensation of vapors are complex. Liquid droplets are formed upon the cooling surface; and if the surface tension of the condensate is relatively low, the droplets form a continuous liquid film. If the vapor contains a noncondensable gas, the fixed gas is carried to the surface by the condensation and remains there as a gas film. The effect of a noncondensable gas on the condensing rate is illustrated by the effect of air on the condensing rate for steam. Othmer[6] reports that the film coefficients between steam at 230°F. and a metal wall are about as follows:

Per cent air	Temperature difference across film, deg. F.		
	10	25	50
0.0	2800	1800	1400
1.07	1500	1000	780
1.96	900	700	570
2.89	740	600	490
4.53	490	420	370

The marked influence of temperature difference on the condensing rate is also shown by Othmer.[7] As an example, at 0 per cent air the condensing coefficient dropped from 10,000 at a ΔT of 1°F. to approximately 1,000 at a ΔT of 80°F. For steam that contained air, the general effect of the temperature difference was the same. Apparently the adoption of a standard average condensation coefficient of 2000 or 3000 B.t.u., as recommended by many authorities, may be in error even for commercial work.

Corrosion, Dirt, and Fouling Resistances.—The practical usefulness of all the foregoing coefficients is vitally dependent upon the condition of the surfaces through which heat is being transferred. With few exceptions the over-all rates computed from the theoretical coefficients can always be reduced by a resistance of 0.0005 (1/2,000). Although this seems small, in certain cases it becomes of great importance. For example, consider heating water at a velocity of 3 ft. per second within tubes by condensing steam. Approximate values of the theoretical film coefficients for these conditions are

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[6] BADGER, W. L., "Heat Transfer and Crystallization, Art. IV," Swenson Evaporator Co., 1928.

[7] *Ind. Eng. Chem.*, **21**, 576 (1929).

$$h_c = 2{,}500$$
$$h_w = 800$$

$$H = \frac{1}{\frac{1}{2{,}500} + \frac{1}{800}} = \frac{1}{0.00165} = 605$$

Inserting a dirtiness resistance of 0.0005,

$$H = \frac{1}{0.00165 + 0.0005} = 465$$

Except in rare cases, a resistance of even 0.0005 is too low, and not infrequently the resistance caused by water-scale, mild corrosion, and dirty liquids amounts to 0.005 ($\frac{1}{200}$). For the foregoing case

$$H = \frac{1}{0.00165 + 0.005} = 150$$

When a definite corrosive action takes place or a solid is deposited at the surface, the resistance may reach a value of 0.033. This magnitude of fouling resistance often results when a cylinder stock is cooled if the average film temperature is below 300°F. Obviously, high velocities tend to keep surfaces clean and reduce the dirtiness factor.

No definite values of fouling resistance can be suggested because each design problem may involve new conditions. However, in Chap. XXI a chart of approximate fouling resistances is given for oil heating and cooling equipments.

Example 39. Transfer Rate in a Steam Heater.—A fuel oil is to be heated from 80 to 150°F. by steam. The oil flows through standard 1½-in. pipe at an average velocity of 4 ft. per sec., and saturate steam at 220°F. condenses on the outside of the pipe.

A. What is the over-all coefficient of heat transfer?

B. How much surface is required to heat 5,000 lb. of oil per hour?

A. The properties of this fuel oil at the average oil temperature are

z = 200 (Fig. 48).
ρ = 58 lb. per cu. ft. (sp. gr. 0.931—A.P.I. 20.5).
c = 0.44 (Fig. 33).

Neglect the difference in area at the inside and outside of the pipe.

On a basis of 1 sq. ft. of surface,

$$H = \frac{1}{\frac{1}{h_o} + \frac{L}{k} + \frac{1}{h_s}}$$

Film coefficient for oil, h_o,

$$\frac{Du\rho}{z} = \frac{1.61 \times 4 \times 58}{200} = 1.865$$

$$\frac{cz}{k} = \frac{0.44 \times 200}{0.078} = 1{,}130$$

$$\left(\frac{cz}{k}\right)^{0.37} = 13.5$$

Using Fig. 66 and extrapolating,

$$\frac{h_oD/k}{(cz/k)^{0.37}} = 33 \text{ approx.}$$

$$\frac{h_oD}{k} = 33 \times 13.5 = 445$$

$$h_o = \frac{445 \times 0.078}{1.61} = 21.6$$

The film coefficient for condensing steam is large, and in this problem it is negligible.

$$h_s = 2{,}500 \text{ approx.}$$

$$\frac{1}{h_s} = \frac{1}{2{,}500} = 0.0004$$

Likewise the resistance of the pipe wall is negligible:

$$\frac{0.145}{12 \times 25} = 0.000484$$

Hence

$$H = \frac{1}{1/h_o} = h_0 = 21.6$$

B. Amount of clean new pipe required:

$$Q = 5{,}000(150 - 80)0.44 = 154{,}000 \text{ B.t.u.}$$

$$\theta = \frac{140 - 70}{\ln {}^{140}\!/_{70}} = 101$$

$$Q = HA\Delta T = 154{,}000 = 21.6 \times A \times 101$$

$$A = 70.7 \text{ sq. ft.}$$

Feet of 1½-in. pipe $= 70.7 \div \frac{5.06}{12} \times 1 = 167$ ft.

A dirtiness factor should be applied to care for the condition of the surface.

CHAPTER XIV

VAPORIZATION AND CONDENSATION

The subject of distillation is usually referred to as a combination operation involving heating, vaporization, fractionation, condensation, and cooling. It is the purpose of this chapter to discuss the theory of vaporization and condensation, and particularly the equilibrium relations for vapor-liquid systems. Both vaporization and condensation are phenomena that involve vapor-pressure, and the two operations can be conducted as analogous processes except that condensation is just the reverse of vaporization. The theory of vaporization must be developed for two component systems, but to be of real usefulness in petroleum refining the theory must be adapted to the treatment of systems involving many components. This is accomplished by the use of the equilibrium-flash-vaporization curve which has been introduced in Chaps. VI and VII.

The physical laws governing the distribution of a component between the liquid and the vapor above the liquid form the basis of many refinery operations. Among these processing operations are shell- or pipestill vaporization, fractionation, and condensation. In addition, the vapor-pressure laws may be applied to the estimation of fractionating-tower temperatures, partial condenser temperatures, and friction losses in tubular heaters and pipestills and in computing the quantity of steam that is required for distillation and steam stripping.

Vaporization and Condensation.—Vaporization may be defined as the change from the liquid to the vapor state. This change absorbs energy. When heat is applied to a mixture of hydrocarbons under constant pressure, part of the energy is absorbed by the change of state and part is expended in raising the temperature of the remaining liquid. This rise in temperature increases the vapor-pressure or the tendency of all components of the mixture to leave the liquid and enter the vapor-phase. Therefore, the vapor from a liquid contains some of each of the components present in the liquid. However, rise in temperature increases the vapor-pressures of the lower boiling components more rapidly than the vapor-pressures of the higher boiling components. Thus the vapor will be richer in lower boiling and poorer in higher boiling components than the liquid that remains, and the residual liquid will be richer in higher boiling and poorer in lower boiling components than the original liquid. Moreover, the vapor will always be richer in lower boiling components than the original liquid, unless the mixture is heated to a temperature at which it is completely vaporized, in which case the vapor will have the same composition as the original liquid. The equilibrium diagram shown in Fig. 67 illustrates these principles. Below the liquid line the mixture is entirely liquid, and above the vapor line a pure vapor-phase exists. Between the two lines a mixture of liquid and vapor is present. Raoult's law was assumed to be valid in computing Fig. 67.

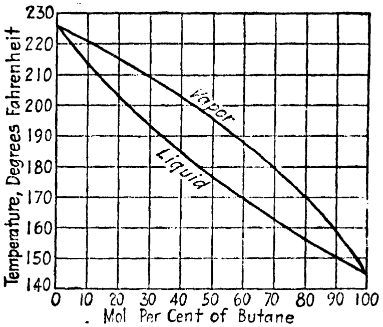

FIG. 67.—Equilibrium phase diagram of butane-pentane at 100 lb. absolute pressure. (Raoult's law.)

These generalizations are equally valid whether the vapor is removed continuously or remains in contact with the liquid. Nevertheless, the manner of separation of the vapor has a quantitative effect on the composition of the distillate and of the remaining liquid.

Condensation is essentially the inverse of vaporization. It follows therefore that the condensate will be richer in higher boiling and poorer in lower boiling components than the original vapor and that the remaining vapor will be richer in lower boiling components than the condensate.

Mechanism of Vaporization.—The most common method of vapor formation is *batch vaporization* as conducted in the A.S.T.M. distillation or as practiced in early shellstill distillation. The mechanism is differential because as the temperature is raised a small amount, a corresponding evolution of vapor takes place. As this vapor is removed and the temperature is again raised, another evolution of vapor occurs. The operation continues thus until finally the liquid is depleted or some extraneous operation such as thermal decomposition occurs. In distilling a liquid mixture thus, each component in the liquid exerts a partial-vapor-pressure or a part of the total vapor-pressure and every component tends to leave the mixture in proportion to its partial-vapor-pressure at that temperature. The lower boiling components, those with high vapor-pressures, compose the most of the first vapors, but some remain in the liquid and are distilled later with other components whose boiling-points are much higher. The reason for this strange behavior may be most easily pictured by conceiving that the high-velocity, low-boiling molecules bump into slower moving molecules and lose the energy content that would normally cause them to leave the liquid and enter the vapor. Some of the slower moving molecules may receive enough energy by these impacts to leave the liquid, and this occurs because we find that high-boiling components are present in the first vapor even though the temperature is much lower than their boiling-points. Thus a mixture of vapors arises throughout the entire distillation.

Differential or batch vaporization may be mathematically formulated as follows. If L represents the liquid, x the percentage of a component in the liquid, and y the percentage of the component in the vapor, a material balance with respect to the component is

$$xL = (x - dx)(L - dL) + ydL$$
$$xL = xL - xdL - Ldx + dxdL + ydL$$

The second order differential $dxdL$ may be neglected:

$$(x - y)dL = Ldx$$
$$\frac{dL}{L} = \frac{dx}{y - x}$$

The quantity that must be distilled in order to cause a particular change in composition may be determined by integrating between L_0, the initial quantity of liquid, and L_1 the final quantity:

$$\ln \frac{L_0}{L_1} = \int_{x_1}^{x_0} \frac{dx}{y - x}$$

The value of the function $dx/(y - x)$ may be obtained by graphically integating between the limits x_1 and x_0. The various values of x are plotted against the corresponding values of $1/(x - y)$, and the area under the curve is the integral of the function. The relation between x and y may be obtained by Henry's law or Raoult's law. Data on two component systems are all that are usually available.

Equilibrium-flash Vaporization.—The mechanism of this type of vaporization differs from differential vaporization in that the vapor is not removed as it is formed but is kept in intimate physical contact with the remaining liquid until the heating is completed. In the refinery such a method is practiced in the pipestill. Any vapor formed in the pipestill tubes is kept in contact with the remaining liquid until the mixture flows from the outlet of the still. Mechanical contacting is effected by the high velocity that results as soon as even a small quantity of vapor is produced.

The flash-vaporization curve may be drawn just as the batch-vaporization curve is drawn, *i.e.*, by plotting the temperature against the percentage distilled (Fig. 68). The molecules that normally would be vaporized at a low temperature are unable to separate themselves from the liquid, and they lose much of their energy content to the high-boiling molecules. Thus vaporization does not start to occur at the boiling-point of the lowest boiling component, and at low percentages vaporized the equilibrium-flash manner of vapor formation requires a higher vapor-temperature than batch vaporization. However, after having vaporized a considerable percentage of liquid, the bombardment of the many high-velocity vapor molecules succeeds in vaporizing a part of the high-boiling material and the flash-vaporization curve crosses the differential-vaporization curve (Fig. 68). At percentages past the intersection, flash vaporization is highly advantageous because a relatively large amount can be distilled without heating to a high temperature.

The saving in heat is not the only advantage. Thermal decomposition halts all distillations at liquid temperatures of approximately 700°F., and thus by flash vaporization the high-boiling part of a liquid may be vaporized, whereas by batch vaporization this high-boiling part could never be vaporized. Of course, steam or a low pressure may be used to distill high-boiling oils, but these modifications can be applied to either method of vapor formation.

Commercial Vaporization.—In practice, the foregoing methods are often used in combination. *Successive flash* vaporization occurs if two or more pipestills are used in series. The liquid residue from the first flash is further heated (or the pressure is reduced), and a second flash-operation is conducted. As an example, crude oil is often heated in an exchanger system and flashed into a fractionating tower. The remaining liquid is then heated in a pipestill and flashed in a second tower. The two-flash atmospheric and vacuum system is also becoming important. In this system the crude oil is heated and flashed at atmospheric conditions and the residue of reduced crude oil (already at a high temperature) is flashed under vacuum to recover gas oil and light lubricating oils. A two-flash system is sometimes used in rerunning brightstock solution. This material consists of approximately 70 per cent low-boiling naphtha and 30 per cent finished brightstock. The naphtha is flashed in one operation, and the remaining brightstock is further heated and flashed in the presence of steam. Other examples are the atmospheric-vacuum redistillation of pressure distillate and the production of well-fractionated solvents by the use of several heaters and fractionating towers.

The *continuous shellstill battery* is an operation involving flash vaporization but not flash vaporization alone. In pure flash vaporization the vapor is physically mixed with the remaining liquid, but in a shellstill battery the flash in each still occurs in the presence of an abnormally large quantity of residue liquid. Thus the concentration of slow-moving molecules is high, and these molecules tend to absorb the energy content of the lower boiling molecules. However, some molecules have energy contents bordering between liquid and vapor, and these molecules are vaporized. The equilibrium that is established is indeed complicated. In a sense, the laboratory batch distillation, with no fractionation, is equivalent to a shellstill battery having an infinite number of stills. Theoretically this method of vaporization seems to have no outstanding advantages. *Batch distillation* as practiced in a single shellstill has been discussed on page 222.

Distillation Curves.—As a summary, a comparison of distillation curves by various vaporization methods will be useful. Figure 68 shows the vapor-temperatures plotted against percentage distilled for (1) flash, (2) A.S.T.M., (3) Hempel, and (4) true-boiling-point distillations of a Mid-Continent pressure distillate. The same relations hold true for other stocks but to a lesser degree for wide-boiling-range materials.

Although the foregoing comparison is commonly used, it appears that the engineer should be more interested in the liquid

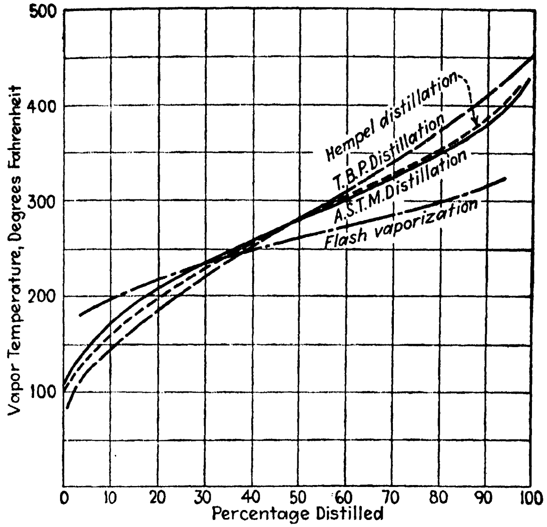

FIG. 68.—Vapor-temperatures for several kinds of distillation.

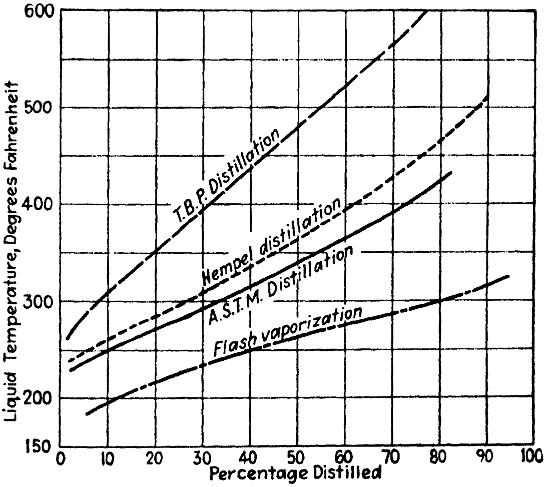

FIG. 69.—Liquid-temperature curves by several kinds of distillation.

temperatures required for a given vaporization than in the vapor-temperatures. Hence the same four curves are compared in

Fig. 69, by plotting the liquid temperature against the percentage distilled. This figure clearly shows that vaporization can be conducted at lower liquid temperatures by flash vaporization than by any other method.

CONDENSATION

In many ways condensation is just the reverse of vaporization, although some of the vaporization mechanisms cannot be mechanically duplicated in condensing equipment. Differential condensation, in which the condensate is removed as soon as it is formed, is not practiced commercially. Differential condensation may be mathematically formulated in a manner analogous to the formulation for differential vaporization.

Equilibrium Condensation.—The mechanism of equilibrium condensation is practiced in most commercial condensers. The condensed liquid is kept in contact with the remaining uncondensed vapor until the outlet of the condenser (or cooler) is reached. The *flash-vaporization* and the *equilibrium-condensation* curves are identical if intimate physical contacting is maintained during both operations.

In large condensers of the tubular type the condenser is usually broken up into several separate condensing units and liquid is withdrawn from each. Each of these units is referred to as a *partial condenser*. However, partial condensation does not give an effective separation between products, and hence it is not generally used as a method of fractionation. The partial condensers that are used in a modern vacuum plant for the separation of gas oil and wax distillate are an exception. This separation need not be exact, and hence partial condensers are satisfactory (Fig. 115, Chap. XIX). In the past, *dephlegmators*[1] or partial-condensation towers, cooled either by air or water, were extensively used. Inasmuch as these equipments are not used now, they will not be discussed further.

In certain plant equipment the vapor is suddenly cooled under equilibrium conditions, and such a process may be called *quench condensation*. Jet condensers embody this method, but they are not widely used. However, barometric condensers, in which steam is condensed with water, are common. Of more importance is the condensation of vapor on each plate of a fractionating tower by reflux. In this case, the condensation may take place in the presence of other vapor that does not condense. As an example, kerosene is condensed on a "side-draw" plate of a bubble-tower. Gasoline vapor is also present at the plate, but it does not condense. The details of the application of this phase of condensation will be discussed in Chap. XXIII. The equilibrium-condensation curve also describes quench condensation.

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[1] The term *dephlegmator* is usually reserved for partial-condenser towers, but certain cracking processes have retained this name for their fractionating towers. They have changed the process of separation but have retained the older name.

EQUILIBRIUM

In order to use any of the aforementioned operations, the equilibrium relations between liquids and vapors must be ascertained. In other words, the distribution of a component in the two phases after no further interchange takes place must be known. For petroleum oil mixtures that contain only a few components, the distribution of a component is accurately described by Dalton's law of partial-pressures, by Henry's law, and in many cases by Raoult's law.

The change of state from liquid to vapor or from vapor to liquid is not unidirectional. Although the predominant tendency may be for the molecules to leave the liquid and enter the vapor, some of the gaseous molecules will reenter the liquid phase. This may be explained by the uneven distribution of energy among the molecules; *i.e.*, although all of the molecules of the vapor are in motion, some have greater energy than others as a result of collisions and other effects, so that the slower molecules fall back into the liquid. Conversely, when the predominant tendency is from the vapor to the liquid state, some of the liquid molecules, which have greater velocity than the average, break from the liquid surface and reenter the vapor phase.

When the rate at which molecules leave the liquid is equal to the rate at which vapor molecules reenter the liquid, the system is said to be in equilibrium and neither vaporization nor condensation appears to be taking place. In reality, both are occurring simultaneously but at equal rates so that the system is in dynamic balance.

Figure 67 shows the equilibrium relationships between liquid and vapor compositions for butane-pentane mixtures at 100 lb.

abs. With the pressure fixed, temperature is the only variable; *i.e.*, there is a single composition of the liquid and of the vapor at each temperature. At equilibrium, a change in the liquid or vapor composition requires a change in temperature, and a change in temperature necessarily involves a change in liquid and vapor composition. For example, assume that a liquid containing 70 per cent butane and 30 per cent pentane is to be heated. No vapor will be formed until the liquid equilibrium line is reached at 163°F. At this point an infinitesimal quantity of vapor will be formed having the composition corresponding to 163°F. on the vapor curve, *i.e.*, 88 per cent of butane. If heating is continued, the composition of the liquid must necessarily change along the liquid curve with the production of increasing quantities of vapor, the composition of which follows the vapor curve. The change in liquid and vapor compositions will continue thus until the total vapor has the composition of the original liquid and the liquid is completely vaporized. Further heating will merely superheat the vapor without changing its composition.

Partial-pressures of Vapor Components.—In a mixture of gases, each gas exerts a pressure equal to the pressure that it would exert if it occupied the entire volume by itself, and the total pressure of the mixture is equal to the sum of the partial-pressures of the component gases (Dalton's law). The pressure exerted by each component is called the partial-pressure[2] of the component and is dependent on the total pressure and the volume or number of molecules of that component in the gas.

In the gas phase if π is the total pressure and y is the volume or mol fraction of an individual component in the mixture, the law of partial-pressures may be expressed as

$$p = \text{partial-pressure in vapor} = \pi y, \qquad \text{or} \qquad \frac{p}{\pi} = y$$

For example, in a vapor mixture composed of 70 per cent butane and 30 per cent pentane at 100 lb. per square inch absolute pressure, the partial-pressures are

$$\text{p.p. butane} = 100 \times 0.7 = 70 \text{ lb. per sq. in.}$$
$$\text{p.p. pentane} = 100 \times 0.3 = 30 \text{ lb. per sq. in.}$$

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[2] Confusion often arises over the term partial-pressure, because it is used in the same discussion both as it is above and also to denote the fraction of the total pressure.

Partial-vapor-pressures of Liquid Components.—Just as each component of a vapor exerts a partial-pressure, each component of a liquid exerts a partial-vapor-pressure. This is dependent upon the concentration of the component in the liquid and the vapor-pressure of the pure component. The escaping tendency of a component appears to depend upon the percentage of the surface area (mol fraction) covered by the component and the molecular energy (vapor-pressure) of the component. If P is the vapor-pressure of the pure component at a given temperature and x is the mol fraction of this component in the liquid,

$$p = \text{partial-vapor-pressure in liquid} = Px$$

Expressed as a fraction of the total pressure,

$$\frac{p}{\pi} = \frac{P}{\pi}x$$

At equilibrium the partial-pressure of a component in the gas is equal to the partial-vapor-pressure of the component in the liquid. Inasmuch as p/π is equal to y, the mol fraction of the component in the gas is

$$y = \frac{p}{\pi} = \frac{P}{\pi}x \text{ (Raoult's law)} \tag{30}$$

Considering two components,

$$\pi y_1 = P_1x_1$$

and

$$\pi y_2 = P_2x_2$$

adding

$$\pi(y_1 + y_2) = P_1x_1 + P_2x_2$$

but

$$x_2 = 1 - x_1, \quad \text{and} \quad y_1 + y_2 = 1$$

$$x_1 = \frac{\pi - P_2}{P_1 - P_2}, \quad \text{and} \quad x_2 = \frac{\pi - P_1}{P_2 - P_1} \tag{31}$$

$$y_1 = \frac{P_1}{\pi}x_1, \quad \text{and} \quad y_2 = \frac{P_2}{\pi}x_2$$

Example 40. Raoult's Law.—A liquid consists of 42.5 per cent butane by volume and 57.5 per cent pentane by volume at 60°F. If the liquid is heated to 180°F. at 100 lb. per sq. in. abs., what will be the composition of the vapor that is produced? (See Example 1, page 29, or Fig. 5.)

Vapor-pressure of C_4H_{10} at 180°F. = 152 lb. per sq. in.
Vapor-pressure of C_5H_{12} at 180°F. = 56 lb. per sq. in.
Sp. gr. at 60°F. of C_4H_{10} = 0.585, and C_5H_{12} = 0.631

Basis: 100 gal. of the mixture. Assume Raoult's law is valid.

$$\text{Mols of } C_4H_{10} = \frac{42.5(8.33 \times 0.585)}{58} = 3.57$$

$$\text{Mols of } C_5H_{12} = \frac{57.5(8.33 \times 0.631)}{72} = 4.20$$

$$\text{Total mols} = \overline{7.77}$$

$$x_1 = \text{mol fraction } C_4H_{10} \text{ in liquid} = \frac{3.57}{7.77} = 0.46$$

$$x_2 = \text{mol fraction } C_5H_{12} \text{ in liquid} = \frac{4.20}{7.77} = 0.54 \text{ or } (1 - 0.46)$$

See Eq. (30):

$$y_1 = \text{mol fraction of } C_4H_{10} \text{ in vapor} = \frac{152}{100}\,0.46 = 0.70$$

$$y_2 = \text{mol fraction of } C_5H_{12} \text{ in vapor} = \frac{56}{100}\,0.54 = 0.30$$

Thus a liquid containing 46 per cent butane and 54 per cent pentane (mol per cent) at 180°F. and 100 lb. per sq. in. is in equilibrium with vapor containing 70 per cent butane and 30 per cent pentane (see Example 41 and also Fig. 67).

Raoult's law is a special case of the more general relationship known as Henry's law. For our purposes Henry's law may be stated as follows:

$$y = Kx \tag{32}$$

The constant K must be determined experimentally, and it is a function of temperature just as vapor-pressure is a function of temperature. It is also dependent on the pressure. In the special case of Raoult's law the value of K is equal to the vapor-pressure divided by the total pressure [see Eq. (30)].

Equilibrium Data.—The actual behavior of complex mixtures is not so simple as may have been inferred from the foregoing discussion. The so-called equilibrium constant designated as K is not a constant in the ordinary sense because it is a function of the kind of material and the amounts and kinds of other materials that are present, of the temperature, and of the pressure.[3] Thus, at the present state of knowledge the values of K must be determined experimentally for each material and for each system in which the material may be present. However, there are particular situations in which the constants can be estimated with some accuracy. In general, Raoult's law [Eq. (30)] may be employed for the normal paraffin hydrocarbons if the pressure is below 60 lb. per square inch.[4] As the pressure approaches the critical pressure of the system, the deviation becomes great and constants such as those shown in Tables 32 and 33[3] and Figs. 70 to 74[4] may be used with more accuracy. At extreme pressures and temperatures no suitable constants or methods are available, but the fugacity method of Lewis and others[5] may be used to gain some idea of equilibrium relations under these conditions. For the special case of gaseous paraffin hydrocarbons in equilibrium with crude oil the data of Katz and Hackmuth[6] are perhaps the best.

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[3] SAGE, HICKS, and LACEY, Tentative Equilibrium Constants for Light Hydrocarbons, A.P.I. Meeting, Wichita, Kans., June, 1938; also *Ref. Nat. Gaso. Mfr.*, July, 1938, p. 350.

TABLE 32.—EQUILIBRIUM CONSTANTS FOR METHANE
(Sage, Hicks, and Lacey)*

Pressure, lb. per sq. in. absolute	At 100°F. for less-volatile constituents of these molecular weights					At 160°F. for less-volatile constituents of these molecular weights					At 220°F. for less-volatile constituents of these molecular weights				
	60	75	100	200	300	60	75	100	200	300	60	75	100	200	300
14.7	....	224	247	259	203	....	247	285	276	226	....	248	293	287	228
20.0	....	165	181	190	149	....	181	210	203	166	....	182	216	211	168
40.0	....	83†	91	96	75	....	91	105	102	83	....	92	108	106	84
60.0	....	55†	61	64	50	....	61	70	68	56	....	61	72	71	56
100.0	....	33†	37	39	31	....	36	42	41	34	....	37	43	43	34
150.0	....	22†	25	26	21	....	25	28	28	23	....	25	29	29	23
200.0	....	17†	19	20	16	....	18	21	21	17	....	19	22	22	18
300.0	11†	12	13	13	11	....	13	14	14	12	....	13	15	15	12
400.0	8†	9	10	10	8	....	10	11	11	9	....	10	11	11	9
500.0	6.56	7.20	7.91	8.22	6.82	6.80	7.74	8.71	8.86	7.40	7.13	8.00	8.93	9.09	7.53
750.0	4.48	5.01	5.48	5.72	4.84	4.60	5.32	5.94	6.18	5.21	4.89	5.52	6.06	6.30	5.33
1,000.0	3.42	3.90	4.29	4.48	3.86	3.46	4.10	4.55	4.84	4.14	3.66	4.24	4.61	4.91	4.23
3,000.0	....	1.17	1.66	2.14	1.78	....	....	1.74	2.15	1.90	....	....	1.66	2.09	2.00

* Only for a system whose less volatile constituent has a viscosity-gravity factor of 0.82.

† Figures rounded out to whole numbers, here and in many other instances.

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[4] BROWN and SOUDERS, Properties of the Paraffin Hydrocarbons . . . , *Oil Gas J.*, May 26, 1932, p. 41.

[5] COPE, LEWIS, and WEBER, *Ind. Eng. Chem.*, **23**, 887 (1931).

[6] Vaporization Equilibrium Constants in a Crude Oil-Natural Gas System, *Ind. Eng. Chem.*, **29**, 1072 (1937).

It must be pointed out that the equilibrium data now available (Tables 32, 33 and Figs. 70 to 74) are not adequate for many conditions and are presented in order to provide a means of illustrating the principles involved in computations. An attempt is made in Tables 32 and 33 to illustrate the effect of the kinds of other components that are present on the constant for the material under consideration, but no information on the effect of the amounts of the other components is available. Although Brown[7] has suggested deviation factors to be used with his equilibrium constants, as given in Figs. 70 to 74, to account for the failure of liquids to behave as ideal solutions, the use of such corrections does not appear to be justified because of other shortcomings of our knowledge.

TABLE 33.—EQUILIBRIUM CONSTANTS FOR ETHANE
(Sage, Hicks, and Lacey)

Pressure, lb. per sq. in. abs.	At 100°F. for less-volatile constituents of these molecular weights			At 160°F. for less-volatile constituents of these molecular weights			At 220°F. for less-volatile constituents of these molecular weights		
	100	200	300	100	200	300	100	200	300
14.7	37.1	38.7	41.2	56.5	55.7	56.9	75.6	77.2	73.7
20.0	27.3	28.5	30.3	41.5	42.5	41.9	55.6	56.9	54.2
40.0	13.8	14.4	15.3	20.9	21.4	21.1	27.8	28.6	27.3
60.0	9.2	9.7	10.3	14.0	14.3	14.2	18.6	19.2	18.4
100.0	5.6	5.9	6.3	8.5	8.7	8.7	11.2	11.7	11.2
150.0	3.84	3.99	4.26	5.73	5.90	5.90	7.56	7.88	7.67
200.0	2.93	3.06	3.28	4.35	4.49	4.52	5.72	6.04	5.90
300.0	2.05	2.13	2.27	2.96	3.09	3.15	3.89	4.13	4.13
400.0	1.61	1.66	1.79	2.30	2.41	2.46	2.96	3.22	3.23
500.0	1.35	1.38	1.50	1.90	2.00	2.07	2.42	2.68	2.71
750.0	1.04	1.04	1.16	1.35	1.46	1.56	1.70	1.93	2.02
1,000.0	....	0.93	1.06	1.09	1.22	1.33	1.35	1.59	1.69
3,000.0	....	0.74	0.93	....	0.83	0.97	....	0.94	1.06

At the present time no constants for the heavier hydrocarbons found in petroleum are available, and hence it can be suggested

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[7] BROWN and KATZ, Vapor Pressure and Vaporization of Petroleum Fractions, *Ind. Eng. Chem.*, **25**, 1373 (1933).

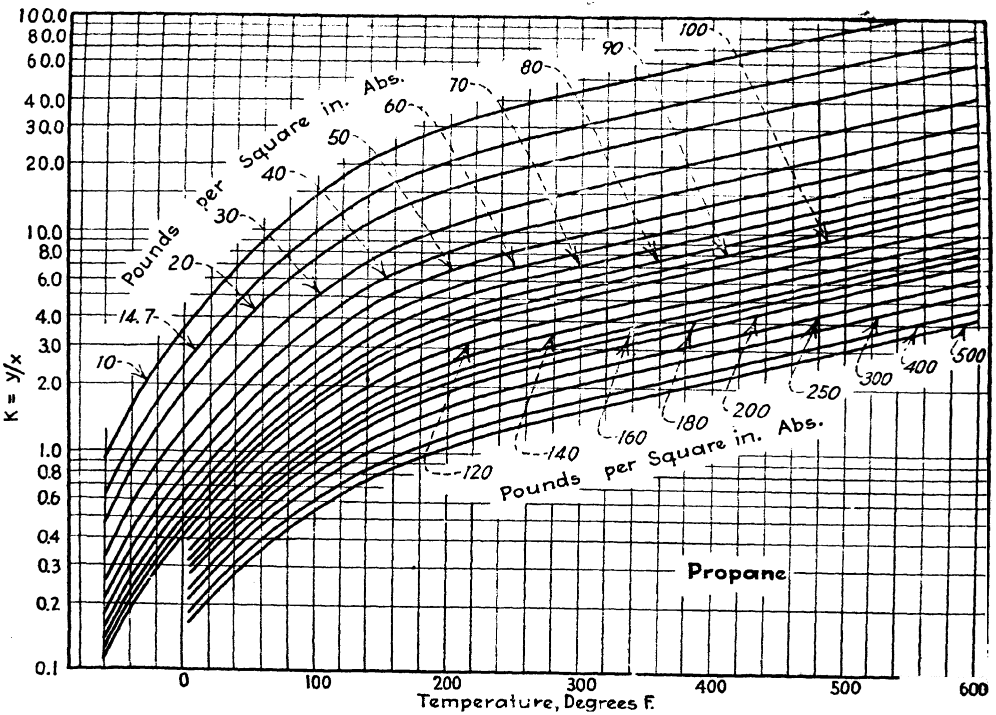

FIG. 70.—Equilibrium constants for propane. (*Courtesy of Dr. G. G. Brown and Ind. Eng. Chem.*)

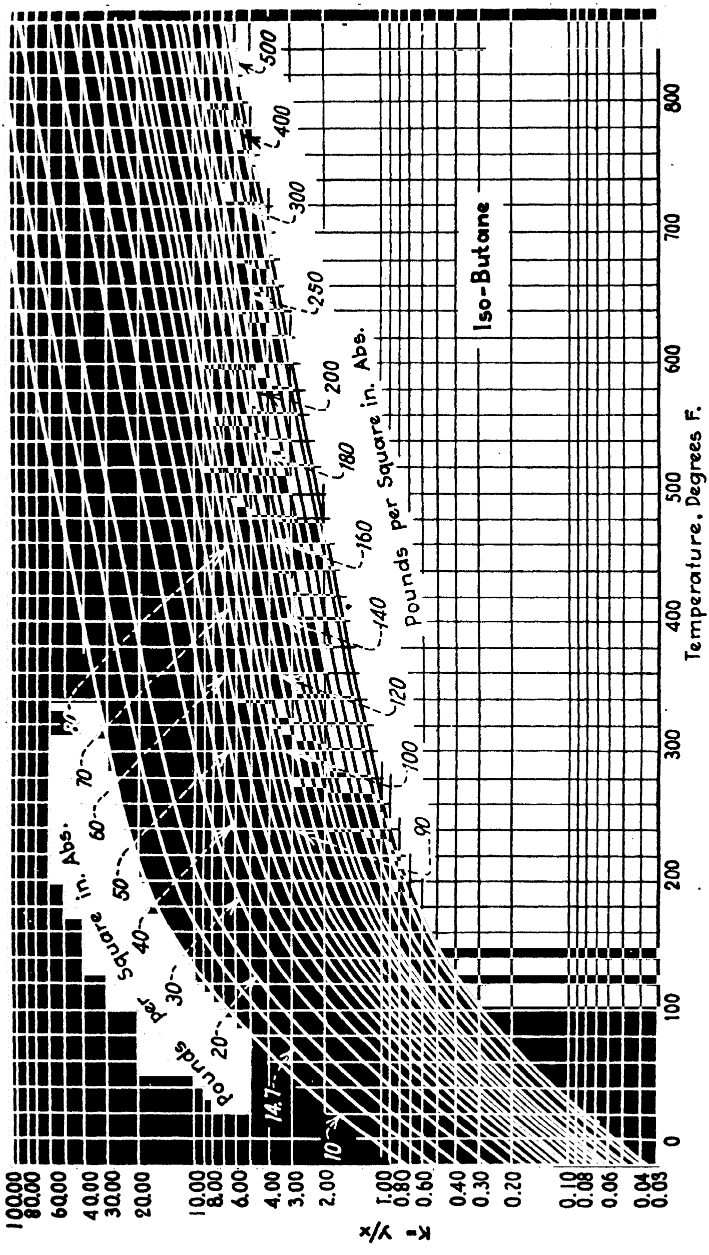

FIG. 71.—Equilibrium constants for isobutane. (*Courtesy of Dr. G. G. Brown and Ind. Eng. Chem.*)

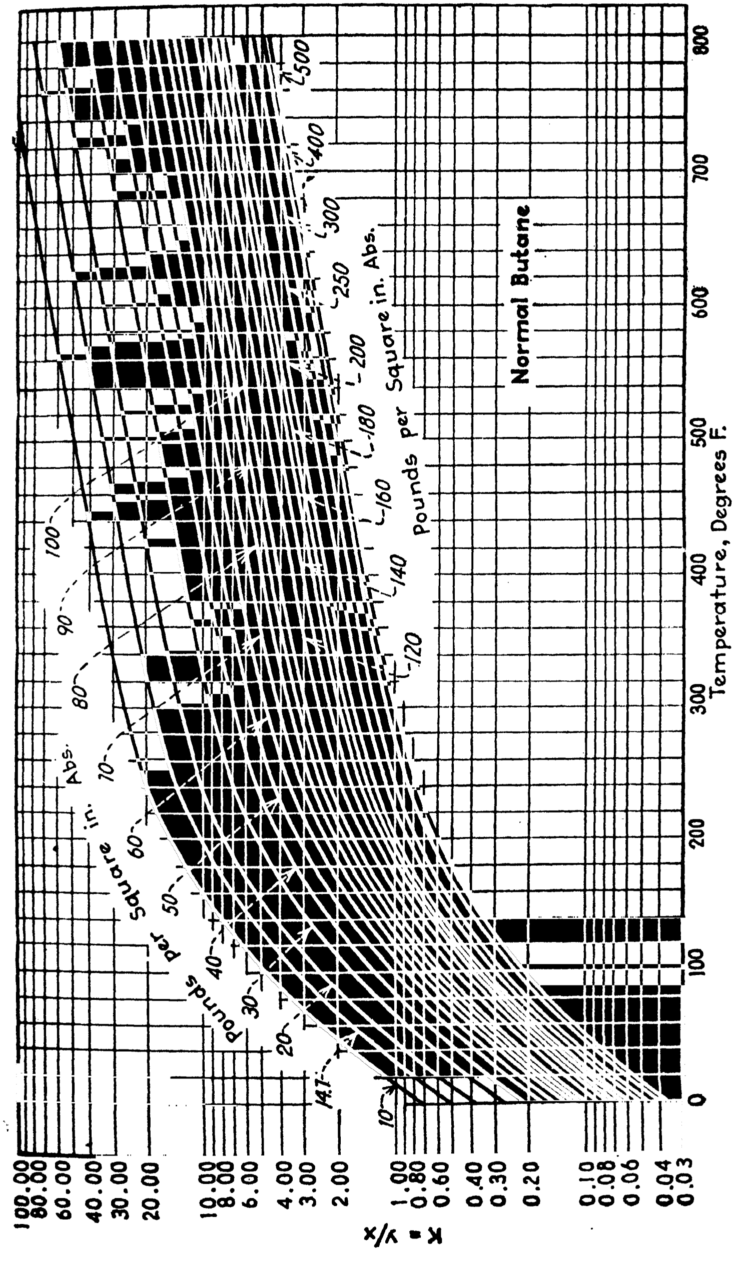

FIG. 72.—Equilibrium constants for normal butane. (*Courtesy of Dr. G. G. Brown and Ind. Eng. Chem.*)

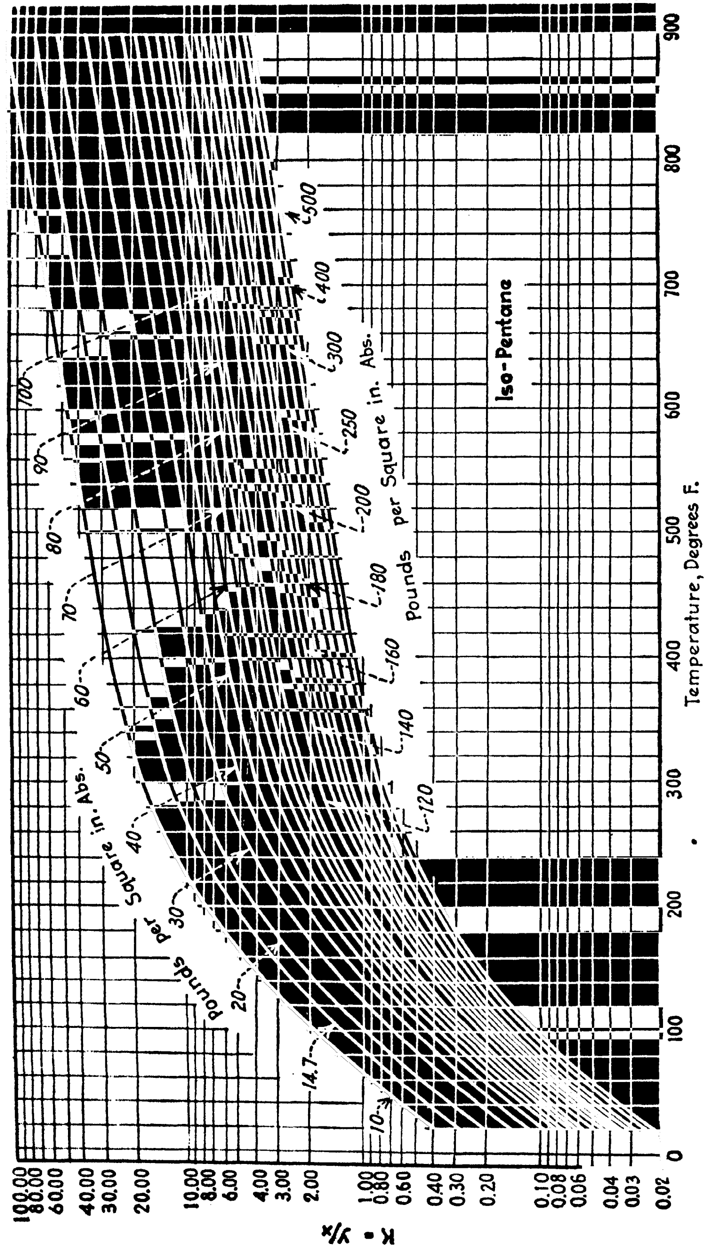

FIG. 73.—Equilibrium constants for isopentane. (*Courtesy of Dr. G. G. Brown and Ind. Eng. Chem.*)

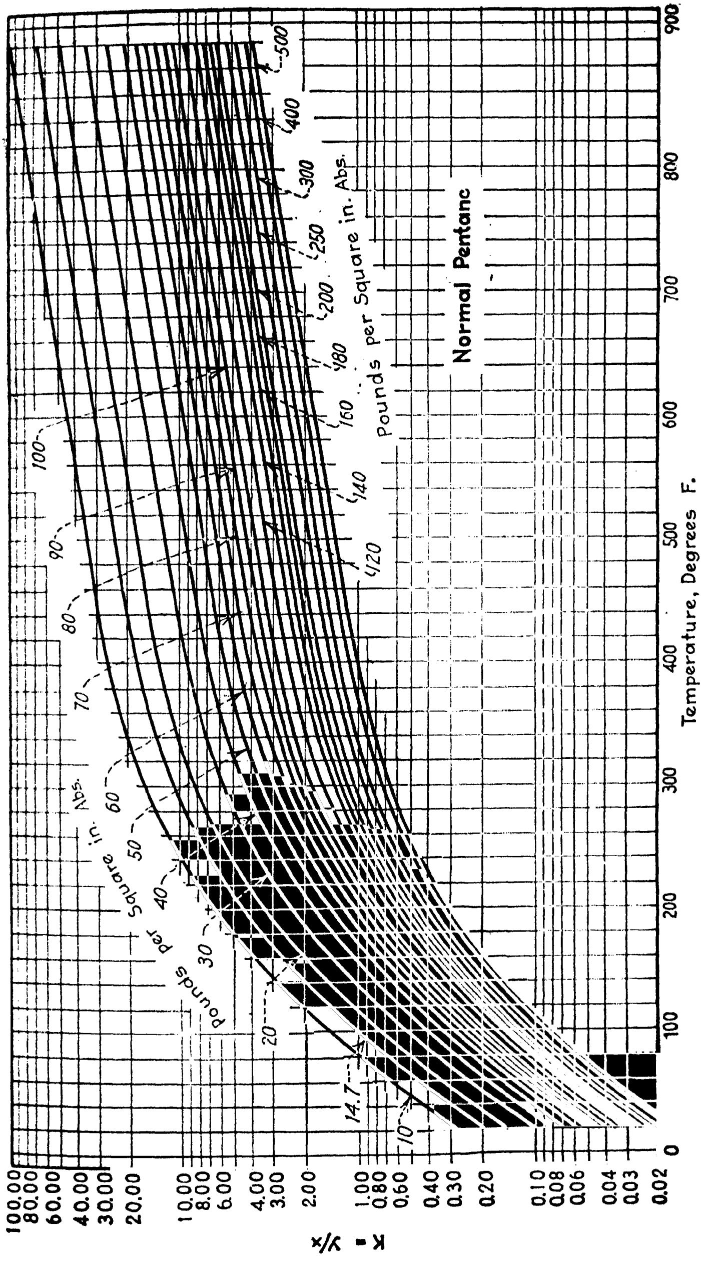

FIG. 74.—Equilibrium constants for normal pentane. (*Courtesy of Dr. G. G. Brown and Ind. Eng. Chem.*)

only that Raoult's law be adopted and that vapor-pressures (Fig. 52) divided by pressure be used as equilibrium constants.

Although Dalton's law of partial-pressures is known to be in error at high temperatures and pressures, no other simple relationship is available.

Example 41. Equilibrium Relations at High Pressures.—Example 40 will be repeated using the actual equilibrium constants rather than assuming that Raoult's law is valid. When the actual constants are used, the compositions of both the liquid and the vapor may be different from those in Example 40. An expression similar to Eq. (30), but using K's, is as follows:

$$x_1 = \frac{1 - K_2}{K_1 - K_2}$$

K_1 for butane (Fig. 72) at 180°F. and 100 lb. = 1.4
K_2 for pentane (Fig. 74) at 180°F. and 100 lb. = 0.6

$$\begin{aligned} x_1 &= \frac{1 - .6}{1.4 - .6} = 0.50 \\ x_2 &= 1 - 0.50 = 0.50 \\ y_1 &= K_1x_1 = 1.4 \times 0.50 = 0.7 \\ y_2 &= K_2x_2 = 0.60 \times 0.50 = 0.3 \end{aligned}$$

It is a coincidence that vapor composition is the same as in Example 40. Note that in this example the 70–30 vapor is in equilibrium with a 50–50 liquid whereas in Example 40 a 70–30 vapor was in equilibrium with a 46–54 liquid.

Equilibrium Relations for Complex Mixtures.—Raoult's and Henry's laws [Eqs. (30 and 32)] may be applied in the same manner as in Examples 40 and 41 to the solution of problems that involve complex mixtures, except that trial-and-error methods must be used. The percentage vaporized at a given temperature can be computed, and the composition of the residue liquid and vapor can also be determined.

Consider 100 mols of a liquid feed-stock called X consisting of X_1, X_2, X_3, etc., mols of the different components designated by the subscripts 1, 2, 3, etc. By equilibrium vaporization of this mixture, by heating to a given temperature at a fixed pressure, V mols of gas is produced which contains V_1, V_2, V_3, etc., mols of the several components. A liquid residue, L mols, is left behind, and it also consists of L_1, L_2, L_3, etc., mols of the several components that constitute the feed.

By a material balance:

Feed-stock..........$X = X_1 + X_2 + X_3 + \cdots$
Vapor..............$V = V_1 + V_2 + V_3 + \cdots$
Residue liquid.......$L = L_1 + L_2 + L_3 + \cdots$

The mol fraction of each component may be expressed as

$$\frac{X_1}{X}; \quad \frac{X_2}{X}; \quad \frac{V_2}{V}; \quad \frac{L_3}{L}; \text{ etc.}$$

Furthermore, for the total material or for any component, material balance equations of this nature may be written

$$X = L + V; \qquad X_1 = L_1 + V_1; \qquad \text{and} \qquad X_n = L_n + V_n$$

Henry's law applied to any component is

$$\frac{V_1}{V} = K_1 \frac{L_1}{L}, \qquad \text{and} \qquad \frac{V_n}{V} = K_n \frac{L_n}{L}$$

or

$$V_1 = K_1 L_1 \frac{V}{L}; \qquad V_3 = K_3 L_3 \frac{V}{L}, \text{ etc.}$$

Substituting $(X - V)$ for L, for each component,

$$V_1 = K_1(X_1 - V_1)\frac{V}{L}, \text{ etc.}$$

Solving for V_1 and simplifying

$$V_1 = \frac{K_1 X_1}{\frac{L}{V} + K_1}, \text{ etc.}$$

Since the sum of the volumes or mols is the total mols of vapor,

$$\frac{K_1X_1}{\frac{L}{V} + K_1} + \frac{K_2X_2}{\frac{L}{V} + K_2} + \frac{K_3X_3}{\frac{L}{V} + K_3} \cdots, \text{ etc.} = V \qquad (33)$$

A similar statement assuming Raoult's law but stated for the liquid residue is as follows:

$$\frac{X_1\pi}{\pi + P_1\frac{V}{L}} + \frac{X_2\pi}{\pi + P_2\frac{V}{L}} + \frac{X_3\pi}{\pi + P_3\frac{V}{L}} \cdots = L \qquad (34)$$

In this equation π refers to the total pressure and P_1, P_2, etc., to the vapor-pressure of each component.

In solving these equations it is necessary to assume a value of L (or V); and by substituting this value, a value of L can be computed. If the computed value is not the same as the assumed value, other assumptions must be made until finally the assumption checks the computed value. By solving the equation for several temperatures, an equilibrium-flash-vaporization curve may be drawn.

A similar equation but for the mechanism of condensation is as follows:

$$\frac{K_1G_1}{\frac{C}{V}+K_1}+\frac{K_2G_2}{\frac{C}{V}+K_2}+\frac{K_3G_3}{\frac{C}{V}+K_3}+\cdots=V \qquad (35)$$

where G_1, G_2, G_3, etc. = mols of each component in original gas.
C_1, C_2, C_3, etc. = mols of each component in condensate.
V_1, V_2, V_3, etc. = mols of each component in final gas.

In solving an equation that contains several variables, there will be as many solutions as there are variables. Perhaps the most reliable method of selecting the true solution is to inspect the vapor-pressures or equilibrium constants of the components. The partition between liquid and vapor will occur at or near the component whose vapor-pressure is equal to the pressure of the system. The method is exact unless one of the equilibrium phases is much larger than the other.

Example 42. Equilibrium Vaporization of Complex Mixtures.—A wild gasoline contains 15 per cent CH_4, 10 per cent C_2H_6, 30 per cent C_3H_8, 5 per cent *i* C_4H_{10}, 10 per cent C_4H_{10}, 15 per cent C_5H_{12}, and 15 per cent C_6H_{14} and heavier materials. Vaporization is conducted at 232 lb. per sq. in. abs. and at a temperature of 100°F. What is the composition of the residue gasoline and of the gas that is vaporized? Basis: 100 mols (or 100 volumes) of gas.

Since Eq. (34), which assumes Raoult's law, is the more complicated, this equation will be used. Note, however, that Raoult's law is not valid at these conditions and that more exact results would be obtained by using Eq. (33).

Inasmuch as the vapor-pressures of C_3H_8 and C_2H_6 are 194 and 750 lb. per sq. in. respectively and the vaporization pressure is 232, the amount of vapor will be something larger than 25 per cent. Assume $L = 70$ (see Table 34, column 3).

For $L = 70$,

$$\frac{V}{L}=\frac{100-70}{70}=0.429$$

Solving for L_3, as an example [Eq. (34)],

P_3 = vapor-pressure of C_3H_8 = 194 lb. per sq. in.

$$L_3 = \frac{X_3\pi}{\pi + P_3(V/L)} = \frac{30 \times 232}{232 + 194 \times 0.429} = 22.0$$

The values of L_1, L_2, L_4, etc., are computed in a tabulated form in Table 34.

TABLE 34

(1) Material	(2) Value of X's, mols	(3) Value of P's, lb. per sq. in.	(4) X's π	(5) P's $\frac{V}{L}$	(6) (5) + π	(7) (4) ÷ (6) L's, mols	(8) (2) − (6) V's, mols
CH_4	15	4,100	3,480	1,755.0	1,987.0	1.75	13.25
C_2H_6	10	750	2,320	321.0	553.0	4.2	5.8
C_3H_8	30	194	6,950	83.1	315.1	22.0	8.0
iC_4H_{10}	5	78	1,160	33.4	265.4	4.38	0.62
C_4H_{10}	10	56	2,320	24.0	256.0	9.06	0.94
C_5H_{12}	15	19	3,480	8.1	240.1	14.5	0.50
C_6H_{14} +	15	4	3,480	1.7	233.7	14.9	0.10
						70.79	29.21

Table 34 shows that the assumption of 30 mols vaporized was not exactly correct but the check was close (29.21). Another assumption and computation is not justified. About 29 per cent will be vaporized at 100°F.

The mol composition of the equilibrium vapor and liquid may be computed by dividing the mols of each component by the total mols

Component	Residue liquid	Vapor
CH_4	2.47	45.37
C_2H_6	5.93	19.85
C_3H_8	31.08	27.39
iC_4H_{10}	6.18	2.12
C_4H_{10}	12.80	3.22
C_5H_{12}	20.49	1.71
C_6H_{14}+	21.05	0.34
	100.0	100.0

Experimental Vaporization Curves.—When such complex materials as gasoline and petroleum fractions are dealt with, the application of the aforementioned equilibrium laws is cumbersome. Furthermore, the component analyses of these heavy oils cannot be easily obtained; and even if such analyses are available, the vapor-pressure data for the compounds are not always available.

At present, the practical way to determine equilibrium relations is by means of experimental flash-vaporization curves and by empirical correlations of these curves.

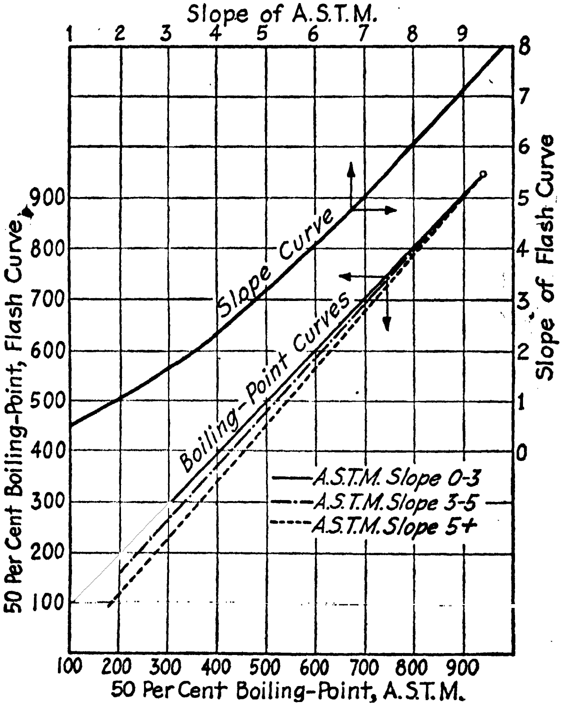

FIG. 75.—Correlation of flash curve and A.S.T.M. (or 10 per cent) distillation curve.

Piromoov and Beiswenger[8] have presented a correlation of flash-vaporization curves. Twenty-two flash-vaporization curves were studied. The empirical correlations shown in Figs. 75 and 76 were derived by the author by the use of the foregoing[8] vaporization data and 42 other flash-vaporization curves.

The term slope, which is used on these two figures, refers to the increase in temperature required to cause an increase of 1 per cent in the quantity vaporized. The slope, on either the distillation or the vaporization curve, is taken between the 10 and 70 per cent points. Of course, it may change along the entire distillation curve, but the 10 to 70 slope is usually a good average for the entire curve. The slope is expressed as degrees per per cent distilled.

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[8] *Am. Petroleum Inst. Bull.* 10, No. 2, Sec. II, p. 52, 1929.

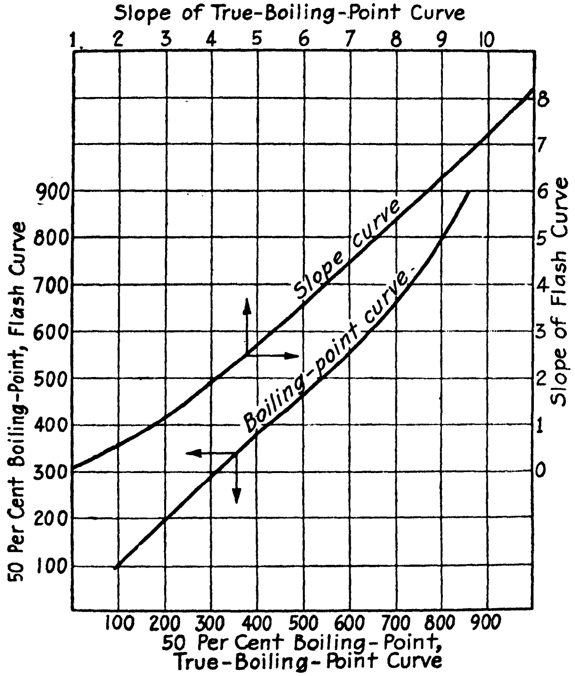

FIG. 76.—Correlation of flash curve and true-boiling-point distillation curve.

For A.S.T.M. distillations of the lighter petroleum products, the computed flash curves are accurate within ±3 per cent throughout the middle of the vaporization curve. The "tails" that are present on the end of the curve introduce an error, but the problem of predicting the curvature of the flash curve will be dealt with later. The correlation of data in Fig. 75 for A.S.T.M. distillations is more exact than in Fig. 76. The superior correlation between nonfractionating (A.S.T.M.) distillations and flash curves may be explained by the semi-flash conditions that exist during the nonfractionating distillation. The A.S.T.M.

distillation actually consists of an infinite number of successive flash vaporizations. The freak behavior of a stock due to an abnormal distribution of compounds or due to the presence of compounds or mixtures that do not behave in accordance with the common laws is at least partly eliminated in the A.S.T.M. distillation. In the true-boiling-point distillation these peculiarities are accentuated.

For relatively simple mixtures for which the component analysis is available, Eqs. (33) and (34) may be used. The equations are solved for several different temperatures to determine the amount of vaporization at each temperature under equilibrium conditions. The series of points constitutes the flash-vaporization curve.

Curvature of Flash-vaporization Curves.—The foregoing correlation method results in a straight-line flash curve. If the distillation curve of the material is substantially a straight line, then the flash curve is also nearly straight. However, most materials have tails or pronounced curvatures at the ends of the distillation curve. If curvature exists, then the flash curve also exhibits a curvature but to a lesser degree. The departure from a straight line may be approximately computed from the curvature of the distillation curve. The deviation from the 10–70 slope that any particular section of the distillation curve may exhibit is directly proportional to the deviation of the actual flash curve from the straight-line flash curve. Thus

$$\frac{\text{Slope of dist. curve, 10–70\%}}{\text{Slope of flash curve, 10–70\%}} = \frac{\text{slope of dist. curve through short range}}{\text{slope of flash curve through short range}} \qquad (36)$$

This method is accurate for those distillation curves which are substantially straight throughout the 10–70 per cent range, but for curves whose slope changes throughout the entire distillation curve the method is not entirely satisfactory. The difficulty probably lies with the inaccuracy of estimating a true average slope and not with the preceding relation.

The flash curves of freak stocks such as brightstock solution and some pressure distillates cannot be determined by these methods. At present the only way to obtain flash-vaporization data for such stocks is by laboratory experiments. Figure 77 indicates the type of flash-vaporization curve that is obtained with unusual stocks.

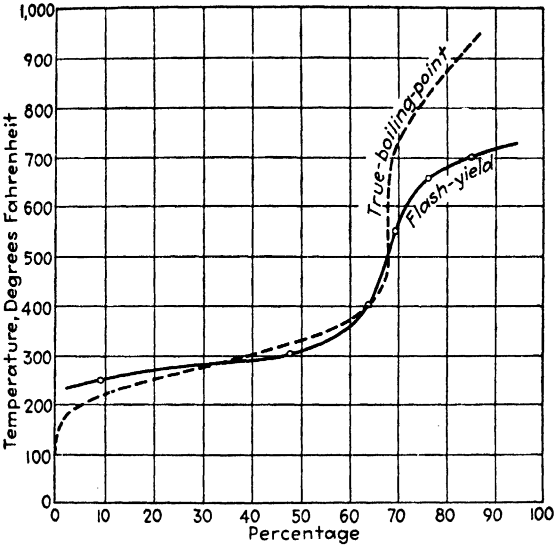

FIG. 77.—Vaporization curves of a Mid-Continent brightstock solution.

Example 43. Curvature of Flash-vaporization Curve.—The experimental flash-vaporization curve and the A.S.T.M. distillation of a pressure distillate are shown in Fig. 80. The computed straight-line flash curve is shown dotted; the triangular points are computed points, and the circle points are experimental ones.

$$\text{Slope of A.S.T.M., 10–70 per cent} = \frac{430 - 170}{60} = 4.34$$

$$\text{Slope of flash, 10–70 per cent (Fig. 75)} = 2.65$$

$$\text{50 per cent B.P. on A.S.T.M.} = 365°\text{F.}$$

$$\text{50 per cent on flash (Fig. 75)} = 335°\text{F.}$$

100 per cent point on linear flash curve,

$$335 + 2.65 \times 50 = 467°\text{F.}$$

As a check, at 0 per cent,

$$335 - 2.65 \times 50 = 203°\text{F.}$$

Computing Curvature:
Ratio of 10–70 per cent slopes

$$\frac{2.65}{4.34} = 0.609$$

Start at the 50 per cent boiling-point, and work in both directions. As an example, the 60 per cent and 45 per cent points will be computed:

Slope of A.S.T.M. between 45 and 60 per cent = 3.46
Slope of flash between 45 and 60 per cent = 3.46 × .609 = 2.11
Temperature at 60 per cent on flash = 335 + 10 × 2.11 = 356°F.
Temperature at 45 per cent on flash = 335 − 5 × 2.11 = 324°F.

The other points were computed as shown in the following tabulation:

Range	Slope of A.S.T.M.	Computed slope of flash	Increment for range	Points on curve
45–60	3.46	2.11	15 × 2.11 = 31.7	324 and 356
60–75	3.06	1.86	28	356 and 384
75–90	3.6	2.2	33	384 and 417
30–45	4.2	2.56	38	286 and 324
15–30	5.45	3.32	50	236 and 286
5–15	7.7	4.7	10 × 4.7 = 47	191 and 236

Equilibrium-flash-vaporization curves may be converted to other pressures than atmospheric by means of Fig. 52 (page 131). Piromoov and Beiswenger[8] conclude that the effect of pressure is to lower or raise the boiling-point just as it does the boiling-points of pure paraffin hydrocarbons. However, they suggest that the correction be made at the point where the two curves cross. They find that the curves cross at the same percentage point regardless of pressure and hence the intersection is the only point that can be accurately used in correcting the flash curve to another pressure.

Separation Obtained by Flash Vaporization.—Not many experiments have been conducted concerning the composition of the vapor and of the liquid that result by flash vaporization. Leslie and Good[9] have studied Cabin Creek Pennsylvania crude oil, and Fancher[10] has studied several other stocks. The distillate contains material that boils above the flash-point, and the residue contains material that boils below the flash-point. The results of these investigators[9,10] are reported in Table 35.

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[9] The Vaporization of Petroleum, *Ind. Eng. Chem.*, **19**, 453 (1927).

[10] The Vaporization of Petroleums and Pressure Distillates, *Petroleum Eng.*, March, 1931, p. 176.

TABLE 35.—SEPARATION BY FLASH VAPORIZATION

Material	Reference	Material in distillate, boiling below flash temperature, per cent	Distillate, boiling below flash temperature, found in residuums, per cent
Cabin Creek crude	9	82.3	11.6
Mid-Continent crude	10	80.8	8.9*
Inglewood, Calif., crude	10	81.6	7.5*
Cabin Creek (successive flash)	9	80.65	16.4

* Approximate.

Fancher finds that for pressure distillates the items shown in Table 35 are not constants; *i.e.*, the higher the flash temperature the poorer the separation. As an example, Fancher's[10] data on shellstill pressure distillate are approximately as follows:

Flash Temperature	Material, in Distillate, Boiling below Flash Temperature
300	76
350	68.5
400	60
450	60

Vaporization in the Critical Region.—Insufficient information is available for determining the exact behavior of mixtures at temperatures and pressures in the critical region, but the general situation is understood. Lines *A* and *B* in Fig. 78 indicate the vapor-pressure lines of two hydrocarbons (*A* and *B*) that compose a mixture, and line *C* may be considered to represent another hydrocarbon that exhibits properties that in most respects represent the properties of the mixture—or better, line *C* represents the molal average vapor-pressure of the mixture and the molal average or pseudo-critical temperature and pressure of the mixture. Critical-points are indicated as *a*, *b*, and *c* respectively.

The gaseous volume of the mixture may be computed for any condition that is not close to the envelope in the diagram, from the pressure-volume-temperature relations of the hypothetical material *C* using the pseudo-critical point designated as

C (Fig. 41, page 111). Lines of constant volume are indicated on the diagram.

The degree of density under various conditions is indicated on Fig. 78 by the blackness or whiteness of each part of the single-phase area. Thus, highly compressed liquids or vapors are shown as dark areas in the left and upper part of the diagram, and the density graduates smoothly to the low-pressure high-temperature area in the lower right corner, which we refer to as a typical or ideal gas region. Note that it is possible by compressing a liquid, heating it, and reducing the pressure to convert a liquid into a gas without conducting vaporization. The common process of distillation is indicated midway on the diagram as a horizontal line or constant-pressure process in which the liquid is heated, vaporization occurs throughout a range of temperature, and finally the vapor may be superheated. In a

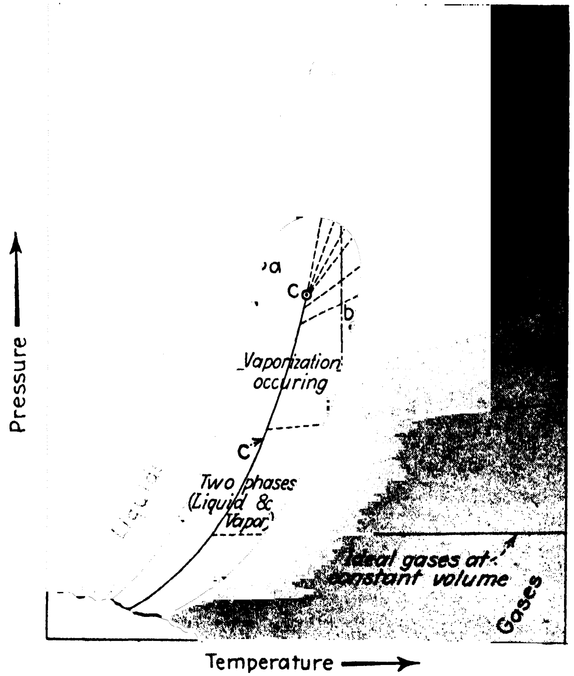

FIG. 78.—Liquid-vapor phase relationship at extreme temperatures and pressures.

similar manner, a constant-temperature expansion (or compression) of a dense fluid is indicated as a vertical line midway on the diagram. In such a process, liquid is produced upon partial expansion, but the liquid vaporizes again upon further reduction of pressure so that nothing but a pure gas phase remains after expansion. This situation has been encountered commercially as *retrograde condensation*. Extremely high-pressure gas wells deposit a maximum amount of condensate when the pressure is reduced to about 1,000 lb. per square inch.

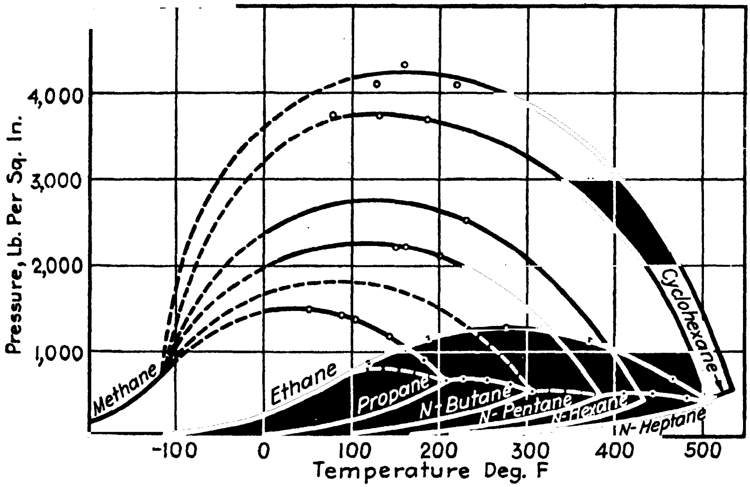

FIG. 79.—The loci of the critical states for a number of binary hydrocarbon systems on a pressure-temperature diagram. (*Courtesy of Ref. and Nat. Gas. Mfr.*)

Little is known about high-boiling mixtures such as those in petroleum oils except that the actual, or true, critical-point of the mixture is at some exceedingly high pressure (over 5,000 lb. in some instances), but some two-component systems have been studied, *i.e.*, methane-propane,[11] methane-*n* butane,[12] methane-*n* pentane,[12] methane-*n* hexane,[12] methane-*n* heptane,[13] methane-cyclohexane,[12] propane-*n* butane,[14] *n* pentane-*n* heptane,[15] ethane-*n* heptane,[16] ethane-*n* butane,[17] and methane-*n* butane.[18] Some of these are indicated in Fig. 79, which was taken from Sage, Hicks, and Lacey.[3] Note that each of the curves on Fig. 79 represents the whole range of composition between 100 per cent of one component and 100 per cent of the other. Thus, for the methane-*n* heptane curve, a whole series of curves could have been shown lying between −120 and 500°F. representing all mixtures between 0 and 100 per cent methane.

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[11] SAGE, LACEY, and SCHAAFSMA, *Ind. Eng. Chem.*, **26**, 214 (1934).

[12] SAGE, WEBSTER, and LACEY, *Ind. Eng. Chem.*, **28**, 1045 (1936).

[13] JOHNSON, Thesis on Vapor Liquid Equilibrium, University of Alberta Library, 1936.

[14] NYSEWANDER, Thesis, California Inst. Tech., 1938.

[15] CUMMINGS, STONES, and VOLANTE, *Ind. Eng. Chem.*, **25**, 728 (1933).

Effect of Steam.—In many petroleum distillations, steam is admitted to the space in which vaporization occurs. The steam reduces the partial-pressure in the vapor by Dalton's law. The boiling-point of a material may be reduced in only two ways. The pressure may be reduced, or some inert gas such as steam may be introduced. In both cases, if the boiling-point is reduced the same number of degrees, the concentration of oil molecules in a unit volume of vapor is the same.

If O denotes the mols of oil vapor, S the mols of steam, p_o the partial-pressure of the oil vapor, p_s the partial-pressure of the steam, and π the total pressure,

$$\frac{O}{O+S} = \frac{p_o}{\pi}$$

and

$$\frac{S}{O+S} = \frac{p_s}{\pi}$$

Dividing,

$$\frac{S}{O} = \frac{p_s}{p_o}, \qquad \text{or} \qquad S = O\frac{p_s}{p_o}$$

but

$$p_s + p_o = \pi$$

and

$$S = O\frac{\pi - p_o}{p_o} = O\frac{p_s}{p_o} \tag{37}$$

The steam need not be bubbled through the oil, although no harm results by so doing. The derivation of Eq. (30) shows that if the partial-pressure in the gas phase is reduced, the partial-vapor-pressure in the liquid must decrease. Thus the use of steam causes vaporization to proceed until the partial-vapor-pressure in the liquid is equal to the partial-pressure in the gas phase.

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[16] KAY, W. B., *Ind. Eng. Chem.*, **30**, 459 (1938).

[17] KAY, W. B., *Ind. Eng. Chem.*, **32**, 353 (1940).

[18] SAGE, BUDENHOLZER, and LACEY, *Ind. Eng. Chem.*, **32**, 1262 (1940).

Gurwitsch[19] and others have reported that steam is more effective in reducing the boiling-point than Dalton's law indicates. Nevertheless, the error that is introduced by the use of Dalton's law in design work is probably not important.

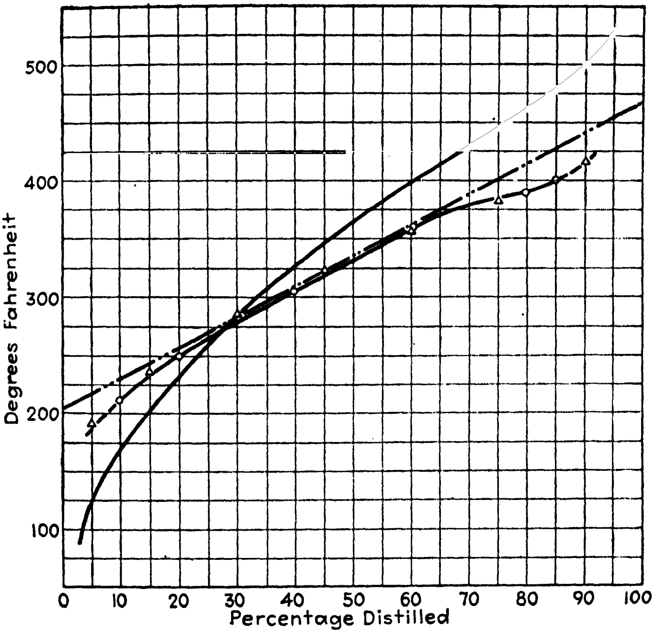

FIG. 80.—Vaporization curves of a pressure distillate.

The foregoing discussion applies primarily to the gaseous phase. The situation in the liquid-phase is different from any situation discussed heretofore, because oil and water are not soluble in each other. In the liquid-phase the water exerts its full vapor-pressure, but each of the mutually soluble constituents exerts only its partial-vapor-pressure as discussed on page 229. If the temperature is high, the vapor-pressure of water is so great that no liquid water exists, but at low temperatures or high pressures an insoluble water-oil system must be handled. In most instances, trial-and-error computations are necessary.

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[19] GURWITSCH-MOORE, "Petroleum Technology," 2d ed., D. Van Nostrand Company, Inc., New York, 1924.

Example 44. Steam Required for Distillation.—A temperature of 370°F. is required to vaporize 65 per cent of the pressure distillate (Fig. 80) by flash vaporization. It is desired to reduce the temperature to 340°F. by means of steam. Vaporization takes place at atmospheric pressure.
Basis: 100 mols of oil vapor.

In order to reduce the boiling-point from 370 to 340°F., the vaporization must be conducted at 490 mm. pressure (Fig. 52, page 131). Enough steam to reduce the partial-pressure in the gas phase to 490 mm. will be used [see Eq. (37)].

$$\frac{S}{100} = \frac{(760 - 490)}{490}$$

$$S = 55 \text{ mols}$$

or

$$= 55 \times 18 = 990 \text{ lb.}$$

If the pressure in the tower were 10 lb. per sq. in. gage,

$$\frac{10}{14.7} 760 + 760 = 1{,}277 \text{ mm.}$$

$$S = \frac{(1{,}277 - 490)}{490} 100 = 158.5 \text{ mols or } 2{,}860 \text{ lb.}$$

APPLICATION OF FLASH-VAPORIZATION DATA

With the possible exception of heat-transfer data, no design fundamental is of more importance and more widespread usefulness than equilibrium vaporization. The equilibrium relations between an oil and its vapor are necessary in the solution of almost all phases of design calculations. For complex mixtures no other relations than the empirical ones shown in Figs. 75 and 76 are available. By following an oil through a complete processing operation the following uses for flash-vaporization data appear:

1. Pipestill-outlet and tower-vaporizer temperatures.
2. Computation of the amount of vaporization in pipestill tubes.
3. Pressure-drop in pipestills (caused by vaporization).
4. Computation of tower plate-temperatures and the top temperature.
5. Heat-transfer rates in vapor condensers.
6. Design of condensers and partial condensers.

Indeed the complete usefulness of this kind of data has not yet been explored. Doubtless during the next few years it will be used in the computation of the number of plates required in heavy oil fractionators. The application of vaporization data to all of these problems cannot be illustrated here, but many of them will be introduced in subsequent chapters.

True-Boiling and A.S.T.M. Distillation Curves.—In applying equilibrium computations to commercial oils, the computations must be based on true-boiling-point data, whereas the finished products are sold on a basis of the A.S.T.M. distillation. For this reason it is necessary to have a relation between true-boiling distillation data and A.S.T.M. data in order to judge the degree of separation that is attained. Such a relationship is shown in Fig. 81,[20] but based on only a few experiments. This figure is used similarly to Figs. 75 and 76 (page 242) except that the slope is established between the 20 and 80 per cent points and the

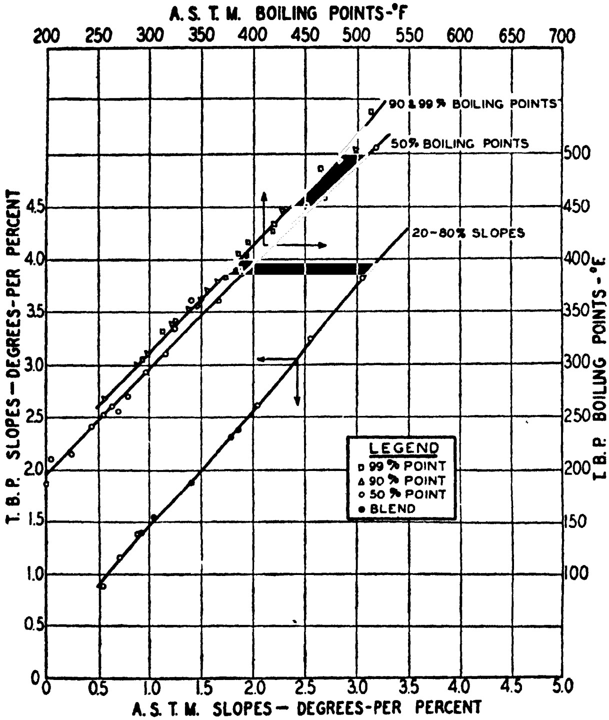

FIG. 81.—Relation of slopes and boiling-points of T.B.P. and A.S.T.M. distillation curves. (*Courtesy of Oil Gas J.*)

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[20] HANSBURG, M., Thesis, University of Tulsa, 1939; also NELSON and HANSBURG, *Oil Gas J.*, Aug. 3, 1939, p. 45.

90 and 99 per cent points have been related as well as the 50 per cent points. No entirely adequate[20] method of correlating the low-boiling end of such curves has been developed, although approximate results can be obtained by the method proposed by Hansburg.[20] A more complete study of this relationship has been published by Geddes.[21]

Successive Flash Vaporization.—The effect of light vapors in aiding to vaporize heavier materials has been aptly referred to as the "carrying-effect of light ends."[8] In the case of successive flash vaporization the carrying-effect of the lighter materials is forcefully evident. A part of the vapor is removed in the first flash, and hence the carrying-effect of this quantity of vapor is no longer available. Owing to the removal of the light vapor, the remaining liquid must be heated for several degrees before additional vaporization occurs. This effect is illustrated in Fig. 82. The same oil as that shown in Fig. 80 was used, but it was vaporized by three successive flash vaporizations.

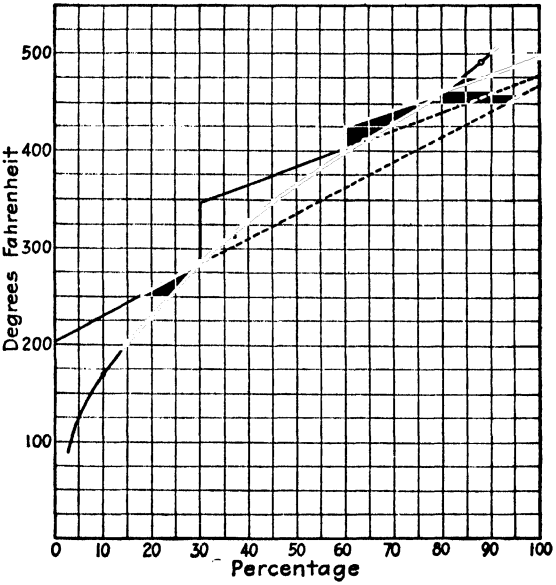

FIG. 82.—Successive flash vaporization.

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[21] GEDDES, R. L., Computation of Petroleum Fractionation, *Ind. Eng. Chem.*, **33**, 795 (1941).

Example 45. Successive Flash Vaporization.

First flash (0 to 30 per cent) (see Example 43).

Second flash (30 to 60 per cent). To avoid confusion, the 70 per cent that remains should be redrawn as 100 per cent.

10–70 slope of dist. $= \frac{457 - 315}{60} = 2.37$
10–70 slope of flash curve $= 1.3$ (Fig. 75)*
50 per cent B.P. of dist. curve = 415°F.
50 per cent point of flash curve = 412°F. (Fig. 75)
100 per cent point $= 412 + 50 \times 1.3 = 477$°F.

* The use of the remaining part of the curve as an A.S.T.M. is not exact.

Third flash (60 to 100 per cent).

10–70 slope of dist. $= \frac{492 - 410}{60} = 1.36$
10–70 slope of flash $= 0.7$
50 per cent point of dist. = 461°F.
50 per cent point of flash = 461°F.
100 per cent point of flash $= 461 + 50 \times 0.7 = 496$

The disadvantage of successive flashing is apparent. For example, to vaporize 80 per cent requires temperatures of approximately 415, 440, and 461°F. respectively by single, double, and triple flash.

Pipestill-outlet Temperature.—If the flash temperature required to vaporize a given percentage of material is, say, 500°F., the pipestill-outlet temperature must be higher than this unless the entire vaporization takes place within the pipestill tubes. Usually the pipestill outlet is under a pressure due to the friction losses in the transfer line, and the pressure suppresses vaporization. As the oil travels through the line, the pressure decreases and vaporization occurs by abstracting heat from the fluid as sensible heat. However, the vaporizer temperature at the outlet of the transfer line is a true flash temperature and may be computed as shown heretofore.

The pipestill-outlet temperature cannot be determined unless the amount of vaporization that has occurred in the pipestill is known.

Example 46. Calculation of Pipestill-outlet Temperature.—A pipestill to be used to distill 65 per cent of the pressure distillate shown in Fig. 80. The tower pressure is 1,100 mm., and by experience with this oil it has been found that the vaporizer temperature of the tower must be reduced with steam to at least 325°F. in order to avoid discoloration.

A. How much steam is required?

B. What will be the temperature at the outlet of the pipestill if no vaporization occurs in the tubes?

C. What will this temperature be if half the vaporization occurs in the tubes?

Basis: 1,000 gal. of pressure distillate per hr.

A A temperature of 370°F. is required to vaporize 65 per cent if no steam is used, and the vaporization takes place at 760 mm. (Fig. 80). This temperature must be reduced by 45°F. (370 − 325). The intersection of the distillation and vaporization curves is at 270°F.

Since flash curves are parallel at different pressures, the flash curve in the presence of steam may be located by determining the partial-pressure required to reduce the temperature by 45°; *i.e.*, the 270 point is corrected to 225°F. From Fig. 52 (page 131) the partial-pressure is 360 mm. For a cracked stock (characterization factor of 11.8),

Molecular weight = 125 (Fig. 35)
Gravity of gasoline = 51 A.P.I. (Fig. 35)
Gravity of butts = 39 A.P.I. (Fig. 35)
Correction for specific heats = none
Mols gasoline $= \frac{1{,}000 \times 0.65 \times 6.455}{125} = 33.6$
Mols steam [Eq. (37)] $= \frac{1{,}100 - 360}{360} \times 33.6 = 69.2$
Lb. steam per hr. $= 69.2 \times 18 = 1{,}245$

B. Pipestill outlet-temperature with no vaporization in tubes. Enough steam will be used to maintain a vaporizer temperature of 325°F. Enough sensible heat above a temperature of 325°F. must be added to supply the heat of vaporization of the gasoline. Vaporization will occur at an average temperature of about 380°F.

Latent heat at 380°F. = approx. 112 (Fig. 37)
Total latent heat $= 1{,}000 \times 0.65 \times 6.455 \times 112 =$ **471,000 B.t.u.**

Assume outlet temperature of 440°F., and check. Use an average of the specific heats of liquid and of vapor, for gasoline.

Gasoline: $1{,}000 \times 0.65 \times 6.455(440 - 325)\,\frac{0.68 + 0.53}{2} = 293{,}000$
Butts: $1{,}000 \times 0.35 \times 6.95(440 - 325)0.637 = 177{,}000$
Total heat from cooling = **470,000 B.t.u.**

The total latent heat should equal the total sensible heat if the assumed temperature is correct. In this case the deviation of only 1000 B.t.u. is sufficiently accurate.

C. Pipestill with 50 per cent of vaporization occurring in the tubes. A.P.I. of material that vaporizes (32.5 to 65 per cent) is about 46.

Latent heat at about 355°F. = 116 B.t.u.
Total latent heat $= 1{,}000 \times 0.325 \times 6.64 \times 116 =$ **250,000 B.t.u.**
Assume pipestill outlet = 390°F.

Sensible heat of one-half gasoline

$$= 1{,}000 \times 0.325 \times 6.64(390 - 325)\,\frac{0.65 + 0.52}{2} = 82{,}000$$

Sensible heat of one-half gasoline (vapor)

$$= 1{,}000 \times 0.325 \times 6.25(390 - 325)0.523 = 68{,}900$$

Sensible heat of butts $= 1{,}000 \times 0.35 \times 6.91(390 - 325)0.625 = 98{,}300$

Total sensible heat $=$ **249,200**

This is also a sufficiently accurate check. The outlet temperature is about 390°F.

Pressure-drop in Pipestills.—The application of flash-vaporization data to the problem of computing the vaporization that occurs within pipestill tubes is complicated by the constantly changing pressure throughout the entire length of pipestill tubing. However, vaporization usually does not occur until the final tubes of the still are reached, because as soon as vaporization starts, the friction loss and the pressure become so high that vaporization is suppressed. In fact a large part of the pressure-drop through a pipestill often occurs in the transfer line from the still to the fractionating tower. To shorten this line does little good because the vaporization is simply pushed back into the still. Likewise a larger transfer line decreases the pressure at the outlet of the still so that more vaporization occurs in the tubes.

The pressure-drop can be estimated by considering the heating coil as being broken up into a series of coils, each of which heats the oil for a temperature range of about 10°F. and operates at a different pressure. By a trial-and-error solution, the length of each section of coil can be computed (working progressively from the pipestill outlet) by assuming the pressure and/or length, computing the vaporization from a flash yield curve at the assumed pressure, and checking the pressure and/or length from the friction loss of the fluid. The method is sound if adequate physical data are available, but it is a tedious procedure.

References

(Older references are given in the First Edition of this book)

KATZ and KURATA: Retrograde Condensation, *Ind. Eng. Chem.*, **32**, 817 (1940).

SAGE, HICKS, and LACEY: Phase Equilibria . . . Methane-*n*-Butane System, *Ind. Eng. Chem.*, **32**, 1085 (1940).

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CHAPTER XV

COUNTERCURRENT OPERATIONS

Many of the unit processes of chemical engineering involve the transfer of a component from one material to another. Examples of such operations are fractionation, absorption, stripping, extraction, and drying. These operations are not always conducted as countercurrent ones, but this manner of operation is usually advantageous.

The three general ways of conducting processes that depend upon equilibrium relations are as follows:

1. *Single-contact or Batch Operation.*—In this method of operation the two materials are mixed or brought in contact with each other in a single operation. After equilibrium is established, the two materials are separated from each other and withdrawn from the system. Batch treatment of an oil with sulfuric acid is an example of a single-contact process.

2. *Countercurrent Multiple-contact Operation.*—This method of operation consists of a number of single-contact operations conducted in a countercurrent manner. The material being brought in contact is treated with contact agent that has been employed in previous contacting stages except in the final stage in which the fresh treating agent is used. As an example, in an absorption system a gas comes in contact with an absorption liquid in a series of treatments as it ascends the absorption tower; the leanest gas is in contact with the lean (or pure) absorption liquid at the top of the tower, and the richest gas is in contact with the richest absorption liquid at the base of the tower (Fig. 88).

3. *Cocurrent Multiple-contact Operation.*—This method is similar to single-contact operation except that the material is repeatedly brought in contact, after separation, with fresh or pure contact agent. This operation is also used in the acid treatment of oils.

Any of these methods can be used for the treatment of a solid with a fluid, but most commercial operations involve the use of two fluids because fluids can be easily handled.

FRACTIONATION

The principles of fractionation have been developed mathematically by a study of two-component systems. Although these derivations are not directly applicable to the fractionation of petroleum oil mixtures, a complete understanding of fractionation cannot be gained without studying two-component systems. In the chemical industries these formulations have proved to be valuable and highly practical.

Fractionation may be broadly defined as any method by which a liquid or vapor mixture may be separated into individual components by vaporization or condensation. The components may be pure compounds; or if the original material is a complex mixture, the components may be products that are still mixtures but whose distillation range is limited by the fractionation process. In a more detailed way the various means of separation have been given special names. *Distillation* is usually considered to refer to a complete operation in which heating, vaporization, fractionation, condensation, and cooling are practiced. *Dephlegmation* is a particular kind of fractionation in which a vapor mixture is separated into components by partial condensation. In this operation the vapor is progressively cooled, and successively lower and lower boiling condensates are collected. The condensate is relatively rich in high-boiling components. At one time the term dephlegmator was used to designate any sort of fractionating tower, but today the meaning of the term is usually restricted to the use herein given. In a more restricted usage the term *fractionation* is used in referring to a countercurrent operation in which a vapor mixture is repeatedly brought in contact with liquids having nearly the same composition as the respective vapors. The liquids are at their boiling-points, and hence part of the vapor is condensed and part of the liquid is vaporized during each contact. By a series of contact treatments the vapor finally becomes rich in low-boiling components and the liquid becomes rich in high-boiling components. The terms *rectification* and *fractionation* are used synonymously.

Vapor-liquid fractionation may be practiced in a bubble-tower or in a packed column. Packed columns are not used extensively in the processing of petroleum, and they will not be discussed in detail. The main disadvantage of the packed column is the channeling of the liquid that occurs as it flows down the tower. Excessive channeling may occur if the diameter of the tower is greater than 18 in. In a bubble column the liquid flows from plate to plate down the column and the vapor bubbles through the liquid on each plate. The plates above the feed point are called rectifying plates, and all of them together are classified as the *rectifying section* of the column. The plates below the feed are called the *exhausting section.* The plates below the feed do not function as exhausting plates unless heat is added to the oil at the base of the column. Hence most petroleum oil columns do not have exhausting sections. The plates below the feed in petroleum columns are usually stripping plates. An exception is the natural-gasoline stabilizer in which the stable gasoline in the base of the column is heated by steam. Occasionally an exhausting section is used in heavy oil systems (see Fig. 106, Chap. XIX, which shows a reboiler system in a pressure distillate rerun unit).

Mechanism of Fractionation.—In computing the degree of fractionation that is accomplished in a particular equipment, the relation between the composition of the liquid and the vapor at equilibrium must be used. Either experimental equilibrium data must be available, or the engineer must compute such data from known laws. Although Raoult's law is valid for only certain conditions, it is about the only general relationship by which equilibrium data can be computed.

Example 47. Equilibrium Relation by Raoult's Law.—[See Eqs. (30) and (31), page 229.] Compute the equilibrium relation of normal pentane and hexane.

$$y_1 = \frac{P_1}{\pi} x_1, \qquad \text{and} \qquad x_1 = \frac{\pi - P_2}{P_1 - P_2}$$

The equilibrium relation will be computed for atmospheric pressure. The vapor-pressure data were obtained from Fig. 5 (page 29). Complete data at a number of temperatures are presented in Table 36. The following computation illustrates how the points in Table 36 were obtained. Equilibrium relation at 120°F.:

Vapor-pressure of C_5H_{12} at 120° = 1160 mm.
Vapor-pressure of C_6H_{14} at 120° = 396 mm.

$$x_1 \text{ for } C_5H_{12} = \frac{760 - 396}{1{,}160 - 396} = 0.477$$

$$y_1 \text{ for } C_5H_{12} = \frac{1{,}160}{760} 0.477 = 0.73$$

TABLE 36.—EQUILIBRIUM DATA FOR PENTANE AND HEXANE

Temperature, deg. F.	Vapor-pressure		760 − P_2	$P_1 - P_2$	x_1 mol fraction	P_1x_1	y_1 mol fraction
	C_5H_{12}, P_1 mm.	C_6H_{14}, P_2 mm.					
97	760	238	522	522	1.0	760	1.0
100	800	255	504	545	0.925	740	0.975
105	895	280	480	615	0.78	698	0.92
110	960	325	435	635	0.685	657	0.865
120	1,160	396	364	764	0.477	554	0.73
130	1,350	478	282	872	0.323	436	0.575
135	1,460	530	230	930	0.248	359	0.476
140	1,600	580	180	1,020	0.176	282	0.371
145	1,750	638	122	1,112	0.109	191	0.252
150	1,900	700	60	1,200	0.050	95	0.125
154.4	2,010	740	20	1,270	0.0157	31.4	0.0414
156	2,150	760	0	1,300	0.0	0.0	0.0

Two common forms of equilibrium diagrams are shown in Figs. 83 and 84. As an example, the vapor from a liquid having a composition of 0.3 mol fraction of pentane contains 0.546 mol fraction of pentane. However, only a very small quantity of this composition of vapor can be produced, because the liquid becomes less rich in pentane as vapor is formed. If the heating is continued, the liquid becomes less and less rich in pentane and

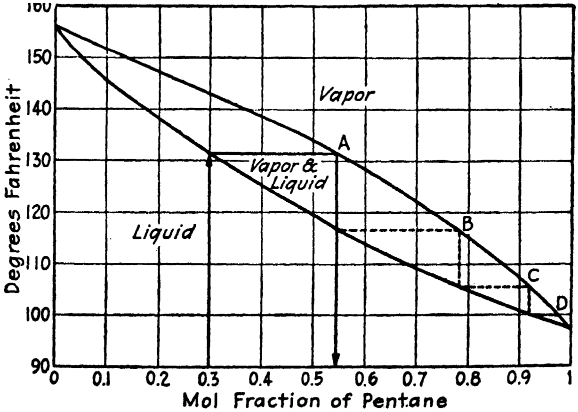

FIG. 83.—Phase diagram for pentane-hexane at atmospheric pressure.

finally, after all the liquid is completely vaporized, the composition of the total vapor is the same as that of the original liquid, or 0.3 mol fraction.

As an illustration, the hypothetical case of the fractionation of an infinitely large quantity of liquid by a series of redistillations will be useful. Consider the series of stills shown in Fig. 85*a*, and compare the compositions with the dotted lines on Fig. 83. An infinite amount of liquid containing 0.3 mol fraction of pentane is heated a fraction of a degree, and a small amount of a vapor containing 0.546 mol fraction of pentane is evolved. This vapor is condensed by cooling it with a liquid that has the same composition as the vapor; and as the liquid is heated, it evolves a vapor having a composition of $y = 0.782$. By repeating this operation several times, a vapor that is almost pure pentane is produced at still *D*. The heating coils in the stills are really unnecessary because the vapor within the coils is of the same composition as the liquid on the outside of the coils and hence the liquid and vapor can be mixed. The same change in composition will result, and the exchange of heat will be much more effective. The bubble-tower shown in Fig. 85*b* is essentially the same as the

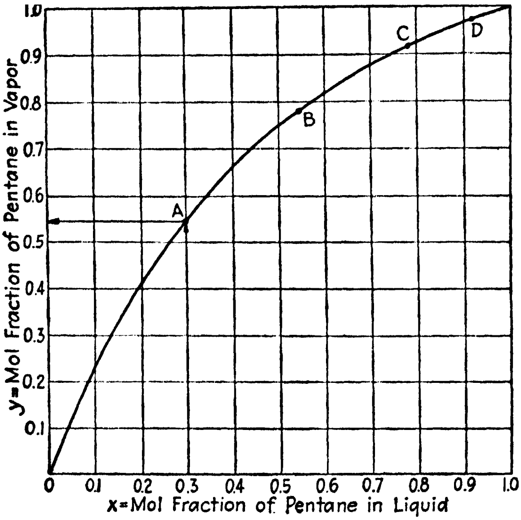

FIG. 84.—Equilibrium relation between pentane-hexane at atmospheric pressure. (See also Fig. 83.)

series of stills except that the liquid from each plate is allowed to flow continuously to the still or the plate beneath. The compositions indicated in Fig. 85 are not practical ones because only a small quantity of purified vapor can be produced but exactly the same principle is utilized in actual fractionating towers. In actual towers a finite amount of vapor or product must be produced, and hence the vapor is not so rich in pentane as indicated in Figs. 83 and 85. Thus more plates are required in actual towers because of the less rich vapor that is produced at each plate and because several bubble plates may be required to produce an equilibrium. The top plate must be continuously fed with a cooling liquid (reflux), or it would soon become dry. The vapor from the top plate is the final product; and hence the reflux must

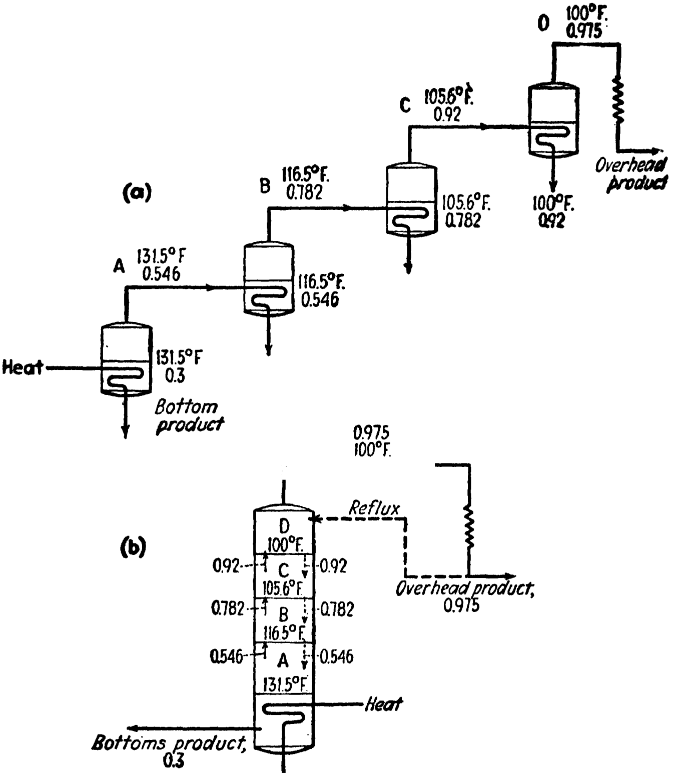

FIG. 85.—Fundamentals of fractionation. (See also Figs. 83 and 84.)

be rich in pentane, or the vapor will be contaminated. Accordingly, the overhead product (0.975) is used as the reflux medium. The reflux flows down the column, but it changes composition from plate to plate so that all of the material that is originally put into the top of the column as reflux is vaporized and returns to the product storage tank.

Theory of Fractionating Columns.—The derivation of mathematical formulae describing fractionation involves several assumptions. In dealing with two-component systems these assumptions are reasonably accurate, but in dealing with complex materials they will introduce serious errors. The most important of these assumptions are as follows: (1) The molal latent heats of all materials are equal; (2) no reflux for cooling the overhead product from the feed-plate temperature is provided.

The molal latent heats of two compounds such as pentane and hexane are about the same. These two compounds are from the same chemical series and are adjacent members of the series. The molal latent heats of butane and heptane are not even approximately the same (see Table 37), and hence, for hydrocarbons that have widely differing boiling-points or that belong to different series, the assumption that the molal latent heat is a constant is inaccurate.

TABLE 37.—MOLAL LATENT HEAT

Compound	B.t.u. per lb.-mol	Compound	B.t.u. per lb.-mol
Ethane	6,300	Cyclohexane	12,900
Propane	8,000	Heptane	13,800
Butane	9,500	Cycloheptane	14,000
i-Butane	9,150	Octane	14,500
Pentane	11,100	Nonane	15,500
2-Methyl butane	11,400	Pentadecane	21,600
Hexane	12,300		

The assumption of equal molal latent heats greatly simplifies the calculations. If 1 mol of vapor (any composition) is condensed, the heat that is removed is just sufficient to vaporize a mol of liquid (at its boiling-point). Thus the number of mols of vapor that travel up the column is the same at any plate provided the feed is introduced as a liquid at its boiling-point. Likewise, the reflux or overflow from plate to plate is a constant amount in each section of the tower (see Envelope II, Fig. 86) because the reflux is equal to the mols of vapor minus the mols of product for the rectifying section and to mols of vapor plus mols of waste for the exhausting section.

Material Balances.—A number of envelopes inclosing parts of a fractionating tower are shown in Fig. 86. According to the first law of thermodynamics, the weight or mols of material going into any one of these systems is exactly equal to the weight or mols leaving that system. The following symbols are used:

F = mols of liquid feed at its boiling-point.
P = mols of liquid product at its boiling-point.
B = mols of liquid residue-product.
R = mols of reflux, at its boiling-point, at any plate above the feed plate.
V = mols of vapor at any plate above the feed plate.
x = mol fraction of lower boiling component in liquid.
y = mol fraction of lower boiling component in vapor.

Subscripts:

p = product from top.
b = residue-product.
f = feed.
n = any plate in rectifying section.
$n + 1$ = plate above the nth plate.
$n - 1$ = plate below the nth plate.
t = top plate.
$t - 1$ = plate below the top plate.
m = any plate in the exhausting section.
s = still.

Envelope I encloses the entire tower system and shows the relation between the feed and the products.

$$F = B + P$$

And for the low-boiling component:

$$Fx_f = Bx_b + Px_p$$

Envelopes II and II′ show the relation among the vapor, reflux, and mols of overhead product:

$$V = P + R, \qquad \text{and} \qquad Vy_t = Px_p + Rx_p \tag{38}$$

Similar equations for the plates below the feed are

$$V' = R' - B, \qquad \text{and} \qquad V'y_s = R'x_{s+1} - Bx_b$$

The change in composition from plate to plate is shown by Envelope III:

$$
\begin{aligned}
Vy_n + Rx_n &= Vy_{n-1} + Rx_{n+1} \\
R(x_{n+1} - x_n) &= V(y_n - y_{n-1}) \\
\frac{R}{V} &= \frac{y_n - y_{n-1}}{x_{n+1} - x_n}
\end{aligned}
\tag{39}
$$

also

$$y_{n-1} = \frac{R}{V}(x_n - x_{n+1}) + y_n$$

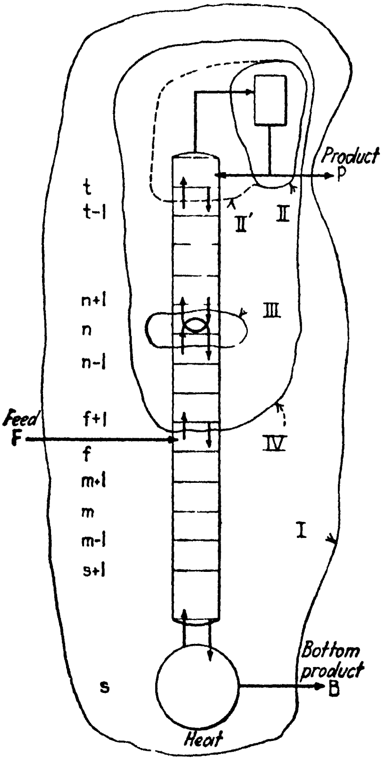

FIG. 86.—Continuous two-component fractionating system.

Minimum Vaporization and Reflux.—The minimum amount of vaporization that is necessary in order to separate a product having a composition x_p is an important quantity. With *minimum vaporization* or reflux, an infinite number of plates are required for the separation. Although this amount of vaporization cannot be used commercially, it is the limiting condition upon which practical vaporizations are based. The other extreme condition is the use of an *infinite* amount of *vaporization.* For infinite vaporization a minimum number of plates is required to effect a separation. The minimum vaporization may be computed as follows (Envelope IV):

$$Vy_f = Rx_{f+1} + Px_p$$

But at minimum vaporization an infinite number of plates are used and the change in composition from plate to plate is very small. Hence x_{f+1} is equal to x_f.

$$V_{\text{min}}y_f = R_{\text{min}}x_f + Px_p$$

But

$$R_{\text{min}} = V_{\text{min}} - P$$

$$V_{\text{min}}y_f = (V_{\text{min}} - P)x_f + Px_p$$

$$V_{\text{min}} = \frac{P(x_p - x_f)}{y_f - x_f} \tag{40}$$

or

$$R_{\text{min}} = \frac{P(x_p - y_f)}{y_f - x_f} \tag{41}$$

In practice, more reflux than the minimum is used. The relative values of x_f and y_f can be found by the equilibrium relation for the compounds that are being separated. The use of a basis of 1 lb.-mol of product P simplifies the computations.

Example 48. Number of Perfect Plates by Mathematical Method.— A mixture of pentane and hexane containing 0.6 mol fraction of pentane is to be fractionated at atmospheric pressure to produce a product containing 0.95 mol fraction of pentane. The feed is at its boiling-point. Use twice the minimum reflex.

How many theoretically perfect plates are required to get the separation? Basis: 1 mol of product [see Eq. (41)].

$$y_f = 0.82 \text{ (Fig. 84)}$$

$$R_{\text{min}} = \frac{x_p - y_f}{y_f - x_f} = \frac{0.95 - 0.82}{0.82 - 0.60} = 0.59$$

Actual reflux:

$$R = 2 \times 0.59 = 1.18 \text{ mols}$$

$$V = 1.18 + 1 = 2.18 \text{ mols [see Eq. (38)]}$$

$$\frac{R}{V} = \frac{1.18}{2.18} = 0.541$$

Considering the top plate [see Eq. (39)]:

$$\frac{R}{V} = \frac{y_t - y_{t-1}}{x_p - x_t}$$

For this plate,

$$y_t = x_p.$$

Also x_t in equilibrium with y_t (0.95) is 0.86 (Fig. 84).

$$0.541 = \frac{0.95 - y_{t-1}}{0.95 - 0.86} \qquad y_{t-1} = 0.901$$

For the $t - 1$ plate,

$$\frac{R}{V} = \frac{y_{t-1} - y_{t-2}}{x_t - x_{t-1}} \qquad y_{t-1} = 0.901$$

$$x_{t-1} = 0.745 \text{ (Fig. 84)}$$

$$0.541 = \frac{0.901 - y_{t-2}}{0.86 - 0.745} \qquad y_{t-2} = 0.839$$

This liquid flowing from this plate has a composition of 0.625. Obviously only a part of another perfect plate is required to complete the rectifying section, because the feed composition is 0.6.

Graphical Method.—The graphical method of solving fractionation problems is usually shorter than the mathematical method used in Example 48. If infinite reflux is used, the composition of the vapor leaving the plate and the liquid arriving at the plate is the same. That is, $y_n = x_{n+1}$; $y_{n+1} = x_{n+2}$, etc. At each plate the composition of the vapor and that of the liquid are related to each other by the equilibrium relation shown in Fig. 84. The equilibrium relation is plotted in Fig. 87 and also a 45-deg. line whose equation is $x = y$. The 45-deg. line is the operating line for the condition of infinite reflux. The operating line relates the composition of the vapor leaving the plate and the composition of the liquid entering the plate. For conditions other than infinite reflux, the liquid composition x does not equal y and the operating line is less steep than a 45-deg. line. The equation of the operating line may be formulated as follows: At the top plate when producing 1 mol of product,

$$\frac{R}{V} = \frac{y_{t-1} - y_t}{x_t - x_p}$$

But $y_t = x_p$

$$\frac{R}{V} = \frac{y_{t-1} - x_p}{x_t - x_n}$$

$$y_{t-1} - x_p = \frac{R}{V}(x_t - x_p)$$

$$y_{t-1} = \frac{R}{V}(x_t - x_p) + \frac{V}{V}x_p$$

But

$$V = R + P$$

$$y_{t-1} = \frac{R(x_t - x_p) + (R + P)x_p}{V} = \frac{R}{V}x_t + \frac{P}{V}x_p \tag{42}$$

This is an equation of a straight line having a slope of R/V and having an intercept on the y-axis of $(P/V)x_p$. Since the operating line extends from (x_p, y_p) to the intercept, the line can also be drawn without using the slope.

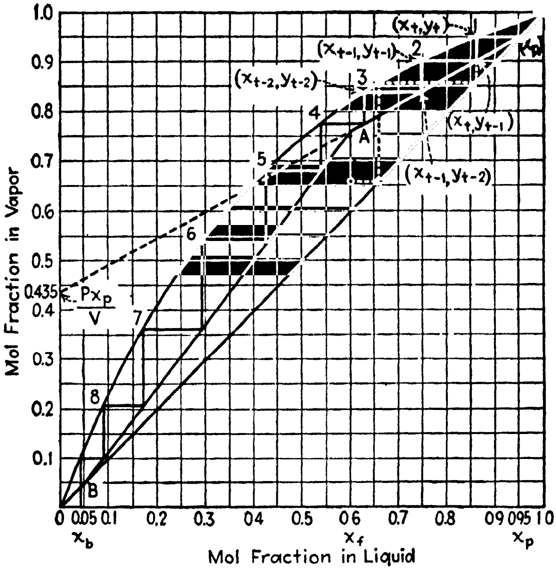

FIG. 87.—McCabe-Thiele diagram for pentane-hexane.

Example 49. Number of Plates by Graphical Method.—Example 48 will be repeated using the graphical method.

The y intercept of the operating line is

$$\frac{P}{V}x_p = \frac{1}{2.18} \times 0.95 = 0.435 \qquad \text{[see Eq. (42)]}$$

The operating line is drawn through the intercept $y = 0.435$, $x = 0$, and through the point x_p, y_t (0.95) (Fig. 87). The number of plates can then be ascertained by drawing horizontal and vertical lines as shown in Fig. 87. Each point on the equilibrium curve indicates one theoretical plate. Thus about 3⅓ perfect plates are required (see Example 48).

The dotted lines indicate the number of plates required at infinite reflux. The operating line for infinite reflux is the 45-deg. line. Only a little more than two plates are required if infinite reflux is used.

Exhausting Section.—The number of plates required in the exhausting section in order to separate a particular bottoms product can be formulated in exactly the same manner as for the rectifying section. However, the computation by graphical methods can be simplified by noting that the exhausting operating line passes through the point *A* (Fig. 87) and through point *B*. Hence the easiest way to handle the exhausting section is to determine and draw the rectifying operating line and then draw the exhausting line. The exhausting line *AB* shown in Fig. 87 is for the separation of a bottoms product having the composition $x_b = 0.05$.

Example 50. Graphical Method for Number of Plates If Feed Is at Center of Column.—Examples 48 and 49 will be continued for a column that is to produce a bottom product $x_b = 0.05$ as well as a top product, $x_p = 0.95$.

The exhausting operating line is drawn as indicated above. The stepwise procedure is continued past the feed composition until the liquid has a composition of 0.05 or less (see Fig. 87). About nine perfect plates are required.

If the plate efficiency is 60 per cent,

$$\text{Actual plates} = \frac{8.8}{0.6} = 14.7$$

The Quantity of Reflux.—As mentioned previously, fractionating towers must operate between two impractical extremes. In one of these the reflux is the minimum that can be used and an infinite number of plates is required, and in the other an infinite amount of reflux is used and a minimum number of plates is required. In practice the engineer must decide whether it pays to purchase a large number of plates or to operate at a higher daily operating cost. The cost of reflux consists mainly of three items: (1) heat to generate the vapor, (2) water with which to condense the reflux, and (3) cost for extra tower diameter.

ABSORPTION

The process of absorbing part of a gas into a substantially nonvolatile liquid is in many respects similar to fractionation. Like fractionation, it depends upon the obtainment of equilibrium between a liquid and a gas. Hence it can also be practiced in a countercurrent manner in bubble-towers or packed columns. It differs from fractionation because the liquid and gas do not exchange places and only the component in which we are interested is transferred from one medium to the other.

In the petroluem industry, absorption processes are usually conducted in a bubble column, and hence the discussion that follows will be limited to this type of equipment. Envelope I (Fig. 88) gives the following material-balance equation:

$$G(y_1' - y_2') = L(x_2' - x_1')$$

$$\frac{L}{G} = \frac{y_1' - y_2'}{x_2' - x_1'}$$

where L = mols of pure absorbent liquid.

G = mols of pure inert gas.

x_1' and x_2' = mols of component per mol of L.

y_1' and y_2' = mols of component per mol of G.

Note that x' and y' are defined differently in the study of fractionation. Here, x' refers to the mols of component per mol of absorbent liquid, whereas in fractionation x referred to mol fraction or the mols of component per total mols of liquid and component. A pound basis as well as a mol basis can be used.

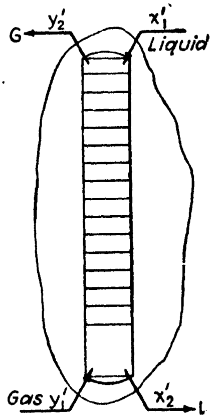

FIG. 88.—Absorption tower.

The ratio L/G corresponds to the ratio R/V that was used in fractionation. The ratio is a constant at all points in an absorbing column and is the slope of the operating line. The operating line has terminals at (x_2', y_1') and (x_1', y_2') and is shown in Fig. 89 as line AB. The transfer of the component from the gas to the liquid is a diffusion phenomenon, and hence the rate of transfer depends upon the difference in concentration of the component in the gas and in the liquid. The transfer of material occurs only when a difference in concentration exists, and hence transfer stops when equilibrium is attained. The minimum amount of absorption liquid that can be used can be determined by noting that the outgoing gas is in equilibrium with the incoming absorbent. The operating line for this condition would intersect the equilibrium line at y_2'. Such conditions would require an infinite number of plates but a minimum amount of oil. In Fig. 89 and in commercial practice, more than the minimum amount of oil is utilized. The number of perfect plates is determined by the stepwise process as indicated in Fig. 89.

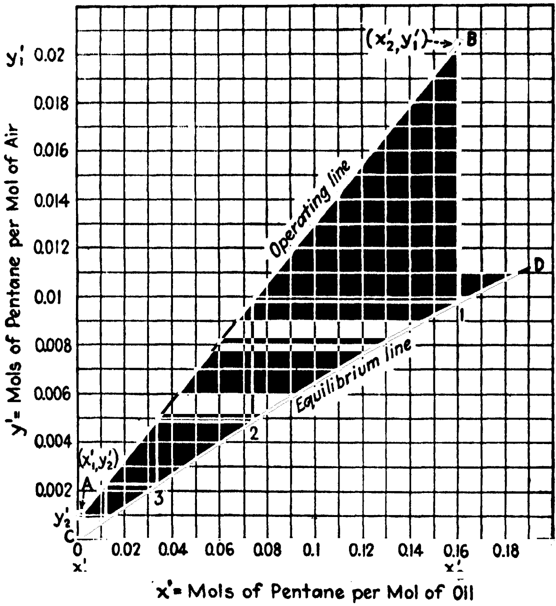

FIG. 89.—Absorption diagram.

The computation of equilibrium data and the solution of an absorption problem are given in Example 51.

Example 51. Absorption of Pentane in Gas Oil.—Air from a solvent plant contains 2 per cent *n*-pentane. The pentane concentration is to be reduced to 0.1 per cent by contacting the gas, at 80°F. and 147 lb. per sq. in. abs., with 6,950 lb. per hr. of an absorption oil that contains 0.05 per cent pentane by weight; 100,000 cu. ft. of the gas, measured at 60°F., is handled per hour. The molecular weight of the oil is 220. Raoult's law and Dalton's law are assumed to be valid at these conditions.

Basis: 1 hr.

Construction of operating line:

Gas entering:

$$\text{Mols air} = \frac{100{,}000 \times 0.98}{379} = 259$$

$$\text{Mols pentane} = \frac{100{,}000 \times 0.02}{379} = 5.28$$

$$y'_1 = \frac{5.28}{259} = 0.0204$$

Gas leaving:

$$\text{Mols pentane} = 259\,\frac{0.1}{99.9} = 0.26$$

$$y'_2 = \frac{0.26}{259} = 0.001$$

Liquid entering:

$$\text{Mols oil} = \frac{6{,}950 \times 0.9995}{220} = 31.6$$

$$\text{Mols pentane} = \frac{6{,}950 \times 0.0005}{72} = 0.05$$

$$x'_1 = \frac{0.05}{31.6} = 0.00158$$

Liquid leaving:

$$\text{Mols pentane} = (5.28 - 0.26) + .05 = 5.07$$

$$x'_2 = \frac{5.07}{31.6} = 0.161$$

These points are plotted as line *AB* in Fig. 89.

Construction of equilibrium line [see Eq. (30), page 229].

$$y = \frac{P}{\pi}x \qquad y = \text{mol fraction in vapor}$$

$$x = \text{mol fraction in liquid}$$

But y' and x' are mols per mol of carrying agent,

$$y' = \frac{y}{1-y} \qquad \text{and} \qquad x' = \frac{x}{1-x}$$

The vapor-pressure of pentane at 80°F. is 532 mm. The relation between x' and y' can be computed as follows:

$$\text{where } x = 0.01$$

$$y = \frac{532}{7{,}600}\,0.01 = 0.0007$$

$$x' = \frac{0.01}{1 - 0.01} = 0.0101$$

$$y' = \frac{0.0007}{1 - 0.0007} = 0.0007$$

x	y	x'	y'
0	0	0	0
0.01	0.0007	0.0101	0.0007
0.02	0.0014	0.0204	0.0014
0.03	0.0021	0.031	0.0021
0.04	0.0028	0.0416	0.0028
0.05	0.0035	0.0525	0.00351
0.07	0.0049	0.0752	0.00492
0.09	0.0063	0.099	0.00635
0.10	0.0070	0.111	0.00705
0.15	0.0105	0.177	0.0106
0.20	0.0140	0.25	0.0142

The number of plates can be computed by the stepwise method. About 3.9 perfect plates are required.

STRIPPING

The process of stripping a component from a liquid by means of a gas may be considered as the reverse of absorption. In absorption the concentration in the gas is high enough to drive the component into the liquid, whereas in stripping the concentration in the liquid is high and the component is transferred from the liquid to the gas. The equilibrium line lies above the operating line (Fig. 90).

Example 52. Stripping Hexane from Absorption Oil with Steam. – A rich absorption oil of the same composition as that produced in Example 51 but containing hexane is to be heated to 267°F. and contacted with 180 lb. per hr. of steam. The tower operates at substantially 267°F. The pressure in the stripper is 1 lb. per sq. in. gage (812 mm.). The vapor-pressure of hexane at 267°F. is 3,800 mm.

Basis: 1 hr.

Construction of operating line:

$$x_1' = 0.00158 \text{ (liquid leaving stripper)}$$
$$x_2' = 0.161 \text{ (liquid entering stripper)}$$
$$y_2' = 0 \text{ (pure steam)}$$
$$y_1' = \frac{5.07}{\frac{180}{18}} = 0.507 \text{ (gas leaving stripper)}$$

These points are used to draw the line AB (Fig. 90).

Construction of equilibrium line: The equilibrium relation will be computed in a different way from that in Example 51 to illustrate another conception.

$$\text{Partial-pressure} = p = Px$$

$$x = \frac{x'}{1 + x'}$$

$$\text{Partial-pressure hexane} = p_p = 3{,}800 \frac{x'}{1 + x'}$$

$$\text{Partial-pressure steam} = p_s = 812 - 3{,}800 \frac{x'}{1 + x'}$$

$$y' = \frac{p_p}{p_s} = \frac{3{,}800 \dfrac{x'}{1 + x'}}{812 - 3{,}800 \dfrac{x'}{1 + x'}}$$

$$y' = \frac{x'}{0.214 - 0.786x'}$$

This equation is plotted as line *CD* (Fig. 90). About 7½ perfect plates are required.

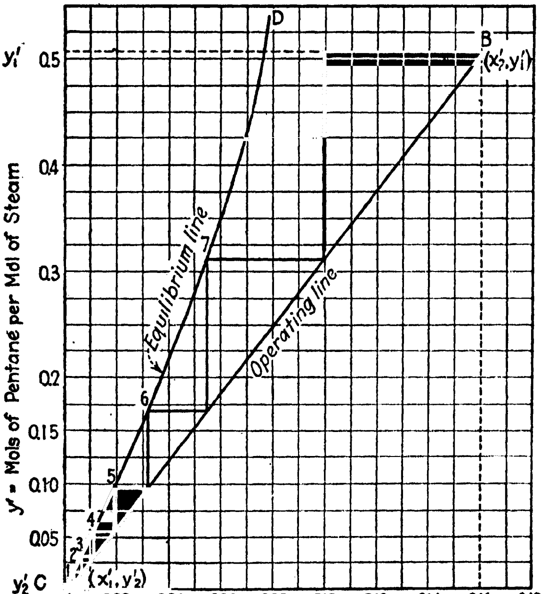

FIG. 90.—Stripping diagram.

EXTRACTION

The process of extraction is used in petroleum refining in the new solvent treating processes for lubricating oils. The low-viscosity-index hydrocarbons, and to some extent the colored materials, are removed from the oil by extraction with a solvent. Thus the operation is the extraction of a component from a liquid by means of the solvent action of another liquid.

Countercurrent processes involve two operations *viz.*, the obtainment of equilibrium and a separation of the contacted materials. The separation of the contacted materials in the operations of absorption and fractionation is relatively easy because one material is a vapor and the other a liquid; but in extraction both materials are liquids, and the separation of these two liquids by settling is the major design difficulty.

The Distribution Law.—This law states that there is a constant ratio between the concentrations of a component that is distributed between two mutually insoluble liquid-phases. The distribution law is really a statement of Henry's law for two liquid-phases.

$$\frac{C_1}{C_2} = K \tag{43}$$

where C_1 = concentration of solute in first liquid-phase, per cent by weight.

C_2 = concentration of solute in second liquid-phase, per cent by weight.

K = a constant that depends only on temperature.

If the solute is a mixture, the law holds for each material in the mixture. Modifications of Eq. (43) to care for dissociation or association will be found in textbooks on physical chemistry.

Equipment Design.—A countercurrent system for a liquid-liquid system is shown in Fig. 91. Although the diagram looks different from the tower systems shown for fractionation and absorption, it involves the same sequence of operations as those used in the liquid-gas systems. The operation can also be practiced in a packed tower or a tower with distributing plates at intervals of 3 or 4 ft. The tower extraction system has the advantage of utilizing gravity to transfer the materials from one stage to the next. It is also claimed that a packed tower of practical height is equivalent to six or seven stages of mixers and settlers.

If W represents the pounds of stock to be treated, S the pounds of pure solvent, x the pounds of component to be extracted per pound of stock, and y the pounds of component per pound of solvent (Fig. 91),

$$W(x_1 - x_2) = S(y_1 - y_2)$$

and

$$\frac{W}{S} = \frac{y_1 - y_2}{x_1 - x_2} \qquad (44)$$

The subscript 1 refers to the incoming liquids, and 2 to the outgoing liquids.

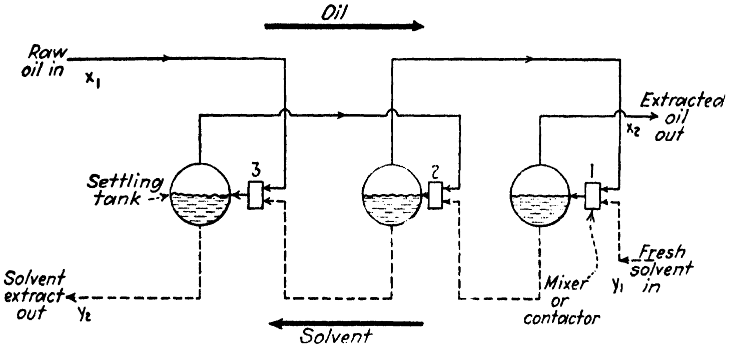

FIG. 91.—Diagram of solvent extraction system.

With conditions for which Eq. (43) is valid, the equilibrium relation in terms of x and y may be formulated as follows:

$$K = \frac{C_1}{C_2}$$

$$C_1 = \frac{x}{1 + x}; \qquad \text{and} \qquad C_2 = \frac{y}{1 + y}$$

$$\frac{y}{1 + y} K = \frac{x}{1 + x}$$

$$y = \frac{x}{K + xK - x} \qquad (45)$$

These equations [Eqs. (44) and (45)] may be plotted exactly as in Fig. 90 for stripping operations, and the number of equilibrium contacts required for the given change in composition of the stock can be computed by the stepwise method. However, the minimum amount of solvent that can be used will be governed by the maximum solubility of the solute in the solvent, as well as the material balance of the system which states that the concentration in the stock must always be greater than in the solvent.

Stokes's law (page 385) for the rate of settling of particles through fluids[1] is valid for the design of settlers, etc.; but inasmuch as the particle size cannot be estimated without empirical tests, the theoretical relationship is of little value. However, it is interesting to note that horizontal settlers are more effective than vertical settlers because the velocity is lower.

Extraction of Oils.—In most practical extraction systems the several components are mutually soluble and hence recourse must be had to triangular coordinate diagrams such as Fig. 92 to show the relation between phases. Such a diagram has three percentage scales, each of which reads from 0 per cent on one side of the diagram to 100 per cent at the apex which is directly opposite. Thus, any point on the diagram represents the percentages of each of the three components of the system.

The phase relationship that is most common for petroleum oil systems is also indicated in Fig. 92. When furfural (or other common solvent) is added to a heavy lubricating-oil stock, two liquid phases (or layers) are produced, one of which (extract) contains a relatively large amount of furfural with some asphaltic material dissolved in it, and the other is lean in furfural (raffinate) but rich in high Viscosity-index oil. On Fig. 92, mixtures of oil and furfural whose compositions fall within the two-phase region bounded by *abc* will separate into two layers whose compositions are shown by the ends of the tie lines labeled 1, 2, 3, and 4; but for all other mixtures the three components are mutually soluble, and no separation occurs. The four tie lines represent experimental data, but additional tie lines can be estimated as necessary.

In all complex mixtures, such as petroleum, it is difficult to define what is meant by pure raffinate (*R*) and pure extract (*E*), and hence the *RE* scale is not read directly in percentages of *R* and *E* but by some significant property such as specific gravity or Viscosity Index. Experimental data are necessary in order to draw the diagrams.

The diagrams are useful in studying single-contact or concurrent multiple-contact operations but are not well suited to the study of countercurrent multiple-contact extractions. Countercurrent extractions can, however, be computed by graphical trial-and-error methods.[2]

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[1] BADGER and MCCABE, "Elements of Chemical Engineering," 2d ed. p. 573, McGraw-Hill Book Company, Inc., New York, 1936.

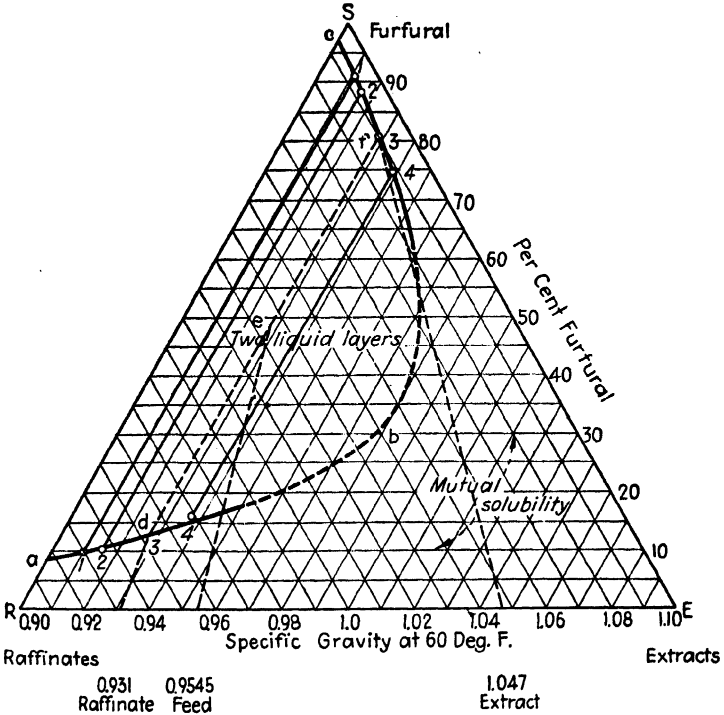

FIG. 92.—Three-component phase diagram at 200°F. for a mixed base oil and furfural. (*Courtesy of Am. Petroleum Inst.*)

Example 53. Solvent Extraction Diagram.—*A*. Addition or removal of solvent involves travel along a line connecting the pure solvent point *S* and a solvent-free oil situated on the base line. Thus, by adding 49 parts of solvent to 51 parts of feed-stock, two layers will separate (see Fig. 92) which contain solvent-free oils having specific gravities of 1.047 (extract) and 0.931 (raffinate).

B. Quantities may be computed by material balances involving either the percentage compositions or the properties of the solvent-free oils contained in the mixtures or may be estimated graphically by the distances along a line connecting the three materials under consideration. Thus, the amounts of the two solutions produced in the separation mentioned above would be about equal because point *e* nearly bisects line *def*. Point *e* falls somewhat closer to point *f*, and hence the raffinate solution designated by point *d* is smaller than solution *f*, amounting by careful measurements or computations to 48 per cent of the total. Likewise, the amounts of solvent-free raffinate and extract can be estimated by distances along the base line. By inspection it appears that the raffinate will amount to about 80 per cent of the feed, or more exactly

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[2] SHERWOOD, T. K., "Absorption and Extraction," McGraw-Hill Book Company, Inc., New York, 1937.

$$100 \times 0.9545 = 0.931R + 1.047(100 - R)$$
$$R = \frac{9.25}{0.116} = 79.7 \text{ per cent}$$

"Science of Petroleum," Vol. III,[3] presents fundamental theory and summarizes experimental data for a number of systems such as those which utilize chlorex, sulfur dioxide, nitrobenzene, cresol, phenol, furfural, benzol-sulfur-dioxide blends, and propane. Triangular coordinate diagrams are also useful in studying solvent dewaxing.[3]

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———, ———, and ———: Conditions at a Liquid-liquid Interface, *Ind. Eng. Chem.*, **29**, 278 (1937).

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[3] DUNSTAN, NASH, BROOKS, and TIZARD, Oxford University Press, New York, 1938.

CHAPTER XVI

CORROSION

All refineries suffer tremendous losses by corrosion. Those refiners who can escape sulfide and acid corrosion by processing selected oils still have the problems of soil corrosion, atmospheric oxidation, and high-temperature oxidation with which to contend. The loss by corrosion in 1928 amounted to about $135,000,000 for the entire petroleum industry and to $50,000,000 in the refinery branch alone. This is equivalent to a levy of about 1 ct. per gallon on each gallon of gasoline that is consumed. In addition to chemical analyses, laboratory methods of determining the corrosiveness of refinery stocks are being developed (refer to Chap. VII, page 97).

Sulfide Corrosion.—Hydrogen sulfide is often found in natural gas or dissolved in crude oil, and in addition it may be formed by the decomposition of organic sulfur compounds at high temperatures. It rapidly attacks steel parts that are exposed to the gas. Equipment that suffers by this corrosion comprises storage tanks and gas lines, and at temperatures exceeding 400°F., pipestill tubes, evaporators, and fractionators. The presence of moisture facilitates the action of hydrogen sulfide, and the concentration of oxygen in the gaseous mixture is of great importance. Devine and others[1] conclude that

1. The presence of oxygen is necessary to cause serious corrosion at normal temperatures.
2. The ratio of oxygen to hydrogen sulfide largely governs the extent of corrosion. A ratio of 114 parts of oxygen per part of hydrogen sulfide causes maximum corrosion. This is equivalent to a sulfide concentration by volume of about 0.87 per cent.
3. Although a dilute sulfide gas is in general more corrosive than a concentrated gas, a minimum concentration of about 0.025 per cent is necessary to cause noticeable corrosion.
4. Corrosion proceeds proportionally with time. This indicates that sulfide scale is of a nonprotective character.

[1] Oxygen Effect on Hydrogen Sulfide Gas Corrosion, *Oil Gas J.*, Apr. 7, 1932, p. 16.

In distillation equipment, sulfide corrosion becomes noticeable at 400° and rapid at 700°F. Thus sulfide corrosion is found to be most active in the hotter parts of distillation equipment such as in the furnace tubes, shellstills, vaporizers, fractionating towers, and hot vapor lines, although certain high-sulfur crude oils have caused corrosion throughout the entire distillation equipment.

The corrosiveness of sulfur-bearing oils is not directly proportional to the sulfur content. Certain organic sulfur compounds decompose at high temperatures evolving hydrogen sulfide, but others do not. Crude oils that contain 2 per cent sulfur and that cause little trouble by sulfide corrosion have been reported, but others containing less than 0.7 per cent have destroyed distillation equipment in less than six months. As a further example, the sulfur content of gasoline marketed in the United States has been limited to less than 0.1 per cent, but in Germany fuels have been sold that contained as much as 1.5 per cent sulfur and no serious engine corrosion was reported.

Chromium steel is the standard material for withstanding sulfide corrosion. Resistance becomes noticeable at about 1 per cent chromium, but in most instances the use of more than 5 per cent is not justified. The approximate rate of penetration of various steels by sulfide corrosion is indicated in Table 38.[2]

TABLE 38.—RESISTANCE TO SULFUR CORROSION

Steel	Relative Depth of Penetration, Carbon Steel Rated as 100 Per Cent
Plain carbon	100
Carbon molybdenum (0.5 Mo)	61
Manganese molybdenum (1.3 Mn–0.3 Mo)	48
1 per cent chromium	58
1.25 per cent chromium* (0.5 Mo–0.75 Si)	62
2 per cent chromium	47
4 per cent chromium	36
5 per cent chromium	33
6 per cent chromium	29
9 per cent chromium	23
13 per cent chromium	18

* Trade-name steel known as DM.

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[2] NELSON, W. L., Evaluating Alloy Steels for Cracking Still Service, *Oil Gas J.*, June 24, 1937, p. 79.

The high-chromium (13 per cent up) steels tend to lose ductility, particularly if used at high temperatures, and hence nickel is frequently employed with the chromium to assist in avoiding loss of ductility.

Neutralizing chemicals, particularly lime, are widely used to combat sulfide corrosion. The effect of ammonia is not entirely known,[3] but caustic soda causes troublesome scaling or clogging of tubes and evaporator surfaces.

Acid Corrosion.—Hydrochloric acid is not present in crude oil, but it may be produced during distillation. It is probably produced by the hydrolysis of chloride salts, particularly magnesium chloride, that are present in the brine found in crude oils. Sulfuric acid is probably produced by the oxidation of hydrogen sulfide in the presence of moisture, but only small amounts of sulfuric acid have been detected. These acids constitute the "acid" corrosion that occurs in vapor lines, condensers, coolers, and run-down lines and particularly at points in which water accumulates, such as in valves in horizontal lines.

The corrosive action of dilute hydrochloric acid at the temperatures encountered in distillation equipment cannot be satisfactorily withstood by any common materials. However, the copper-base alloys have been widely used for hydrochloric acid and brine corrosion. Although conditions are not the same in all plants, the use of copper-base alloy tubes for condensers and water-cooled exchangers appears to be increasing. One refiner[4] has been using the following kinds of tubes:

	Percentage of tubes in service			Approx. relative costs
	1930	1933	1936	
Steel	18.0	16.3	12.0	1.0
Stainless steel (18–8)	60.3	14.9	5.6	4.8
Admiralty metal or other copper-base alloys	21.7	68.8	82.4	1.2

Ammonia is unsuitable as a neutralizer if copper-base alloys are used, because it may destroy the metal faster than acid corrosion.

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[3] PUCKETT, R. E., Preventing Corrosion, *Oil Gas J.*, Sept. 23, 1937, p. 44.

[4] WILTEN, H. M., *Mining Met.*, March, 1937, p. 143.

The other neutralizers appear to produce protective films so that corrosion halts after an initial action. If scale-forming water is used, admiralty-metal tubes must be cleaned frequently, because corrosion occurs mainly beneath breaks or porous spots in the scale. The zinc in the brass is dissolved and is replaced by spongy copper.[5]

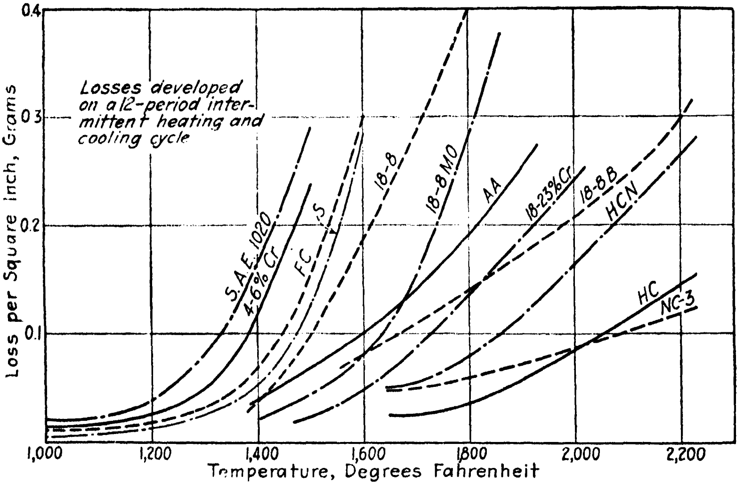

FIG. 93.—Oxidation of alloy steels at high temperatures. (*Courtesy of Republic Steel Company.*)

Oxidation.—Iron and steel oxidize or rust in the presence of air or moisture. At high temperatures such as those encountered in boilers and furnaces, oxidation or scaling occurs very rapidly. This type of corrosion is so common that it does not always receive the attention that it deserves. The chromium and chrome-nickel steels are excellent resistors to high-temperature oxidation, and at the same time they retain their strength and toughness at elevated temperatures. For these reasons they are admirably suited for boiler and furnace parts that are exposed to high temperatures and to furnace gases. Figure 93 shows the relative scaling resistance of the common chromium steels.[6]

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[5] PEW, A. E., Minimizing Corrosion in Condensers, *Oil Gas J.*, Apr. 16, 1931, p. 112.

[6] ANON., Alloy Steels . . . Refining Equipment, *Ref. Nat. Gaso. Mfr.*, April, 1933, p. 140.

These data were obtained by 12 intermittent heating and cooling cycles.

	Steel	Carbon	Chromium	Nickel	Silicon
Plain	1020	0.20			
Enduro	4-6	0.20 max.	4.0– 6.0	....	0.50 max.
Enduro	FC	0.12 max.	12.5–15.0	....	0.50 max.
Enduro	S	0.12 max.	12.5–15.0	....	0.50 max.
Enduro	18-8	0.16 max.	16.5–20.0	7.0–10.5	0.75 max.
Enduro*	18-8-Mo	0.16 max.	18.0–22.0	7.0–10.5	0.75 max.
Enduro	AA	0.10 max.	15.0–18.0	....	0.50 max.
Enduro	20-23	0.20 max.	18.0–23.0	....	0.50 max.
Enduro	18-8-B	0.18 max.	16.5–19.5	8.0–10.5	2.0–2.5
Enduro	HCN	0.20 max.	22.0–25.0	10.0–13.0	0.75 max.
Enduro	HC	0.20 max.	25.0–30.0	....	0.50 max.
Enduro	NC-3	0.20 max.	23.0–27.0	17.0–21.0	2.00 max.

* 2.0–4.0 Molybdenum.

Alloy steels containing a high percentage of special element are expensive, and there has been a tendency to use the low-percentage steels, such as 4-6 chromium (or with 0.5 molybdenum), for parts of equipment that are not exposed to the most severe conditions. Pipestill tubes can be constructed of 4-6 chromium steel, but supports that are not cooled must be constructed of high-percentage alloy steels.

Sulfuric Acid and Acid Sludge.—The universal materials for handling sulfuric acid are steel and lead. Ordinary mild steel withstands concentrated acid, but lead must be used for dilute acid. Lead is such a ductile material that it presents many structural difficulties. For this reason, lead-lined rather than solid lead equipments, such as pipelines, agitators, and pumps, are gaining in favor. Recently some success has been attained in spraying steel with lead. A number of other materials including tin, zinc, aluminum, copper, brass, nickel silver, monel metal, and stainless steel are also being used. The coating[7] is applied by roughening the surface by a sand blast and spraying the surfacing metal from an oxyacetylene gun. Several coats must be applied.

Certain alloy cast irons such as Duriron (14.5 silicon) and the high-silica irons are useful for lines, valves, pumps, etc., for handling sulfuric acid and acid sludge. In fact, ordinary cast iron is used for many corrosive conditions because of its cheapness.

[7] Rice, H. B., Metal Spraying . . . , *Ref. Nat. Gaso. Mfr.*, April, 1933, p. 148.

Neutralizing Chemicals.—Few materials are satisfactory resistors to "acid" corrosion, and hence neutralizing chemicals such as ammonia, sodium hydroxide, sodium carbonate, and lime are widely used. In general, these chemicals are introduced into the vapor lines of distillation units. Ammonia is introduced as a gas, and the other materials as dilute solutions, although lime is preferably added as a slurry. Lime is often used in cracking plants by injecting it with the charge to the pipestill, and it serves partly to reduce sulfide corrosion as well as acid corrosion.

The solutions are usually injected into the system by direct-acting pumps. A fine dispersion of the chemical in the oil is essential, and hence the solutions are often mixed with a part of the oil by means of mixing columns before they are injected into the system. These columns consist of a pipe containing baffle plates. From 0.15 to 0.3 per cent by volume of caustic soda solution (about 10°Bé.) or 0.3 to 1.0 lb. of lime per barrel of charging-stock is usually sufficient, although the exact amount must be determined by plant experiments. Obviously, an excess of the neutralizer creates alkaline corrosion, which may be more severe than the original acid corrosion, and hence the chemicals are not added in large enough quantities to neutralize the acid or sulfide materials completely. The corrosion can often be reduced to half by adding much less chemical than the amount required for complete neutralization.

Ammonia rapidly attacks admiralty metal, and hence ammonia should not be used in a system having brass condenser tubes or parts. In some instances ammonia has been successfully used with admiralty-metal condensers but under careful supervision so that no large excess was ever present. Ammonium chloride gradually accumulates in the lines and condensers, and it must be "flushed out" with water or steam during cleaning periods. Caustic soda also causes deposits, and these deposits are so difficult to remove that the use of caustic has been gradually abandoned. Caustic deposits are particularly troublesome within fractionating towers so that if acid corrosion occurs within a tower, ammonia has usually been adopted as the neutralizing agent. Caustic soda also causes caustic embrittlement of the steel shells of evaporators, towers, etc. Two and one-half to twenty pounds of anhydrous ammonia is used for 1,000 bbl. of crude oil, depending upon the amount of acid that is produced. Some refiners have reported a decrease of 97 per cent in the extent of acid corrosion by the use of ammonia.

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CHAPTER XVII

THERMAL DECOMPOSITION (CRACKING)

The thermal decomposition, or cracking, of oil was called to our attention by Silliman[1] in 1871 and ever since commercial application in about 1910 the study of the theory of cracking has proved difficult. The complex composition of heavy oils has at times made the task seem almost unsurmountable. Even today, only a few of the hydrocarbons that boil above 200°F. have been isolated and studied. Hence the development of our great cracking facilities has been made mostly along other lines than fundamental theory.

Although data on cracking are not so complete as we desire, they are complete enough to permit definite conclusions concerning almost any phase of cracking. The purpose of this chapter is to present and correlate, as completely as possible, the data that are available.

Mechanism of Cracking.—Cracking is a phenomenon by which large oil molecules are thermally decomposed into smaller lower boiling molecules; at the same time certain of these molecules, which are reactive, combine with one another to give even larger molecules than those in the original stock. The more stable molecules leave the system as cracked gasoline, but the reactive ones polymerize, forming tar and even coke. Although gasoline is the common light product from cracking plants, all of the oils having boiling-ranges intermediate between fuel oil and gasoline are also produced. However, these intermediate materials are kept within the cracking system until they are decomposed, and they normally do not appear as final products. These intermediate materials, called recycle stock, can be kept in the cracking system until they are decomposed, by recycling them in a continuous system or by operating a batch system under a high pressure. The production of intermediate stocks is illustrated by the following general chemical reactions:

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[1] *Am. Chem. Soc. J.*, **2**, 18 (1871–1872).

Charge-stock.................................... $C_7H_{15}{\cdot}C_{15}H_{30}{\cdot}C_7H_{15}$
↓ *heavy gas oil*
Cracked stock.............................. $C_7H_{16} + C_{14}H_{28}{:}CH_2 + C_6H_{12}{:}CH_2$
↓ *gasoline* + *recycle stock* + *gasoline (antiknock)*
More cracking.............. $C_2H_6 + (C_4H_8{:}CH_2 + C_8H_{18} + C_6H_{12}{:}CH_2) + CH_2{:}CH{\cdot}CH{:}CH{\cdot}CH_3 + C_2H_4$
↓ *gas* + *gasoline* + *gum forming materials* + *gas*
Polymerization........................... $C_2H_6 + (C_4H_8{:}CH_2 + C_8H_{18}) + C_{12}H_{22} + C_2H_4$
gas + *gasoline* + *tar or recycle* + *gas*

Although these exact reactions probably do not take place, they are representative of the over-all reaction that occurs during cracking.

Thus two general types of reactions take place: (1) primary reactions in which decomposition of large molecules into small molecules takes place and (2) secondary reactions by which active products polymerize to form heavy tarry materials. At the same time the products of polymerization may be again decomposed into smaller molecules. The nature of the primary reactions may be illustrated by the experimental work of Hurd and Spence[2] on the decomposition of n-butane at 600°C. (1112°F.). Their work indicates that the major part of the cracking occurs by these two reactions:

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \rightarrow CH_4 + CH_3{\cdot}CH{:}CH_2$$

and

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \rightarrow CH_3{\cdot}CH_3 + CH_2{:}CH_2$$

"At 600 degrees the first of these appears to proceed to the extent of about 55 per cent and the second to 40 per cent. Dehydrogenation reactions into butene or butadiene appear to represent less than 5 per cent of the total." The dehydrogenation reactions referred to are

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \rightarrow H_2 + CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$$

and

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \rightarrow 2H_2 + CH_2{:}CH{\cdot}CH{:}CH_2$$

Their work also indicates that the tendency to dehydrogenate, leaving an olefin with the same number of carbon atoms as the original paraffin hydrocarbon, rapidly diminishes as the series is ascended. Thus the production of large amounts of hydrogen by cracking gas oil stocks should not be expected.

The olefin hydrocarbons are not usually found in raw petroleum stocks, and hence the decomposition of olefins should properly be

[2] *J. Am. Soc.*, **51**, 3353 (1929).

considered as a secondary decomposition reaction. Both hydrogenation and dehydrogenation may occur during the decomposition of olefins. Diolefins, paraffins, polymers, new olefins, hydrogen, and probably many other materials are produced. As an example of diolefin and paraffin formation, pentene-1 reacts thus:

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \rightarrow CH_4 + CH_2{:}CH{\cdot}CH{:}CH_2$$

and

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 + H_2 \rightarrow CH_4 + CH_3{\cdot}CH_2{\cdot}CH{:}CH_2$$

The secondary reactions by which polymers are formed may be illustrated thus:

$$CH_2{:}CH_2 + CH_2{:}CH_2 \rightarrow CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 \text{ (dimer)}$$
$$CH_3{\cdot}CH_2{\cdot}CH{:}CH_2 + CH_2{:}CH_2 \rightarrow CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2 \text{ (trimer)}$$

or

$$RCH{:}CH_2 + R'CH{:}CH_2 \rightarrow \text{tars, oils, etc. (polymers)}$$

The data of Wheeler and Wood[3] on butene-1 illustrate the over-all results of all of the foregoing types of reactions (see Table 39).

TABLE 39.—DECOMPOSITION OF BUTENE-1*

Temp., deg. C.	Calc. contact time, sec.	Per cent by weight of butene-1 heated			Gas analysis, per cent by volume of butene-1 heated						
		Total liquid	Distillate up to 170°	C	H_2	CH_4	C_2H_6	C_2H_4	C_3H_6	C_4H_8	C_4H_6
600	61.5	12.9	6.5	Nil	0.8	8.1	1.9	3.2	7.6	54.1	0.9
650	58.2	29.8	20.3	Nil	6.2	37.2	7.1	14.2	24.5	19.8	1.7
700	55.	35.8	23.6	Trace	11.9	62.1	10.6	22.3	19.6	2.1	1.4
750	52.5	39.6	22.4	Trace	17.3	78.5	9.7	31.4	5.6	1.3	0.2
800	50.	39.4	19.9	1.0	27.2	89.	7.6	30.2	2.0	1.0	
850	47.7	35.	16.2	4.7	50.5	95.7	6.1	20.6	....	1.0	
900	45.7	13.9	7.8	7.1	85.2	103.3	5.0	9.6	....	0.9	

* Wheeler and Wood.

In general, at higher temperatures the production of fixed gases, such as methane and hydrogen, increases (Table 39) and the polymerization reactions appear to decrease. How true these generalizations are for high-molecular-weight hydrocarbons and particularly for naphthene hydrocarbons cannot be stated, but we expect that they are equally true.

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[3] *J. Chem. Soc.*, p. 1819 (1930).

The general reactions of the paraffin hydrocarbons may be summarized as follows:

Decomposition:

$$R{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}R' \rightarrow R{\cdot}CH{:}CH_2 + CH_3{\cdot}R'$$
$$R{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3 \rightarrow R{\cdot}CH{:}CH_2 + CH_4$$
$$R{\cdot}CH_2{\cdot}CH_3 \rightarrow R{\cdot}CH{:}CH_2 + H_2$$

Polymerization:

$$R{\cdot}CH{:}CH_2 + R'{\cdot}CH{:}CH_2 \rightarrow \text{tars, etc.}$$

Frolich and Fulton[4] conclude that the paraffin hydrocarbons are least stable and that others follow in the order olefins, diolefins, naphthenes (six carbon ring), naphthenes (five carbon ring), and aromatics. This applies to cracking temperatures of 750 to 1100°F. and to compounds of the same molecular weight. At higher temperatures the diolefins become more stable than the naphthenes, and hence the diolefins and their condensation products can be produced at high temperatures.[5] Egloff[6] and his associates have made a thorough study of the technical literature on the thermal reactions of hydrocarbons.

Properties of Cracked Materials.—The properties of the products that are produced by cracking depend greatly upon the extent of cracking that is practiced. Sachanen and Tilicheyev[7] have studied the mechanism of cracking by producing recycle stocks that had been cracked once, twice, and several times. In each cracking test the oil was cracked at 450°C. The fraction boiling between 200 and 350°C. was separated by distillation and subjected to another cracking operation at 450°C. The extent of cracking was not exactly the same for each recycle oil, but the qualitative comparison (Table 40) is useful. Note the

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[4] The Theory of Cracking, "Science of Petroleum," Vol. III, p. 2104, Oxford University Press, New York, 1938.

[5] Frolich, Simard, and White, *Ind. Eng. Chem.*, **22**, 240 (1930).

[6] "Reactions of Pure Hydrocarbons," Reinhold Publishing Corporation, New York, 1937.

[7] *Oil Gas J.*, Dec. 19, 1929, p. 48.

30.6 A.P.I., 392°F. gasoline that was produced from the sixth recycle stock.

TABLE 40.—CRACKING TESTS OF EMBA (RUSSIAN) GAS OIL*

No. of operation	Time, min. at 450°C.	Yield per cent by weight		A.P.I. gravities		
		Below 200°C. (392°F.)	Above 350°C. (672°F.)	Cracking-stock and recycle oils	Below 392°F.	Above 672°F.
1	42	28.7	10.5	30.8†	58.2	10.6
2	52	21.3	8.6	28.2	52.5	1.05‡
3	75	16.3	7.9	23.8	46.0	1.116‡
4	101	12.1	10.3	19.2	38.4	1.177‡
5	101	3.9	12.4	15.4	37.1	1.157‡
6	160	8.0	19.0	14.5	30.6	1.243‡

* See footnote 7.

† Emba gas oil (uncracked).

‡ Specific gravity.

Sydnor and Patterson[8] have studied a Mid-Continent gas oil, and cycle oils produced from it, in a similar manner. Their experimental equipment simulated plant operations more accurately and they present more complete data than Sachanen and Tilicheyev.[7] They attempted to operate for the formation of a fuel oil of the same gravity in each cycle of cracking. They aimed to produce a 400°F. end-point gasoline and a 10 A.P.I. tar in each cycle. Their results are given in Table 41. Note that the viscosity of the 10 A.P.I. tars ranged from 210 for the first tar to 18 for the tar produced in the fourth crack. The insoluble sediment in the fuel oil increased from 0.018 to 0.37 for the same tars.

Egloff[9] reports the analysis of straight-run and cracked gasolines (from the same crude oil) as shown in Table 42. This table indicates that the percentage of paraffin (knockers) and of naphthene hydrocarbons is less in cracked gasolines than in straight-run gasolines but the percentage of unsaturated and of aromatic (antiknock) hydrocarbons is greater.

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[8] *Ind. Eng. Chem.*, **22**, 1237 (1930).

[9] *Petroleum Eng.*, Midyear, 1930, p. 104.

Cracked gasolines have higher octane numbers than straight-run gasolines from the same parent stock. Gasolines from normal stocks usually have octane numbers between 67 and 80; but if the stock is naphthene base, such as many Coastal, California, Texas, and Mexican stocks, the octane number of the cracked gasolines may be between 80 and 90. Higher octane numbers are obtained by operating at high temperatures and high pressures, and the octane number, when cracking is accomplished by vapor-phase processes (temperature 1050 to 1250°F.), may be as high as 100.

TABLE 41.—EXPERIMENTS ON RECYCLING

Yields	Run 1 straight-run gas oil	Run 2 cycle gas oil from Run 1	Run 3 cycle gas oil from Run 2	Run 4 cycle gas oil from Run 3	Built-up yields	Yields on straight-run gas oil currently recycling
400°F. gasoline*	24.3	19.3	16.7	14.9	47.8	48.2
Cycle gas oil*	63.5	66.2	67.5	67.1	19.1	22.3
Fuel oil*	4.4	7.3	8.6	11.0	15.7	19.1
Gas†	5.5	4.2	4.5	5.5	11.7	12.7
Coke†	0.5	0.3	0.7	1.5	1.2	1.7
Total†	96.3	96.4	97.4	99.0	92.6	100.2
Operation:						
Conversion-per-pass	24.3	19.3	16.7	14.8	.....	21.3
Properties:						
Gas oil gravity	33.7	30.4	28.9	26.5	24.7‡	
Fuel oil gravity	10.0	12.0	9.0	8.5		
Fuel oil, Furol visc. at 122°F.	210.0	22.0	25.0	18.0		
Fuel oil, insoluble sediment, per cent	0.018	0.26	0.26	0.37		

* Per cent by volume.
† Per cent by weight.
‡ Cycle oil from Run 4.

Recent work on the reforming of straight-run gasoline has added much to our knowledge of the factors that affect the octane number. LeRoi and Ferguson[10] find that the smaller the yield of gasoline and the greater the loss by producing gas the higher the octane number. Their experimental work was conducted in a modified tank-and-tube equipment. They introduce the term degradation, which may be defined as the percentage decrease in the yield of total liquid products for an increase of 1 in the octane number. General conclusions from their work are given in Table 43.

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[10] Developments in Naphtha Reforming Practice . . . , 3d Midyear Meeting, A.P.I., Tulsa, Okla., May, 1933.

TABLE 42.—CHEMICAL ANALYSES OF GASOLINE

Gasoline	Unsaturated hydrocarbons	Aromatic hydrocarbons	Naphthene hydrocarbons	Paraffin hydrocarbons
Pennsylvania, straight run	2.5	Trace	14.9	82.6
Pennsylvania, cracked	16.8	23.1	12.1	48.0
Mid-Continent, straight run	2.9	3.9	19.7	73.6
Mid-Continent, cracked	15.0	18.5	12.6	53.0
California, straight run	2.2	10.4	28.1	58.0
California, cracked	25.8	10.8	19.8	43.6
Smackover, cracked	14.7	27.5	21.2	36.6
Cushing, Okla., straight run	1.6	4.9	23.7	69.8
Cushing, Okla., cracked	10.9	19.8	18.0	51.3
Somerset, Ky., straight run	3.8	5.3	20.6	70.3
Somerset, Ky., cracked	12.5	14.9	11.8	60.8
Straight-run gasoline from Rumanian crudes as follows:				
Bustenari	3	13.3	29.0	54.7
Arbanasi	4	24.0	14.0	58.0
Ceptura	2	7.2	20.1	70.7
Arbanasi	....	15.7	21–23	61.3–63.3
Moreni	....	23.3	16.2	60.5
Rumanian cracked gasoline:				
After chemical treatment	9.7	28.9	17.4	44.0
Before treatment	19.0	23.5	14.6	42.9

More exact values are given in the original paper,[10] and a comparison indicates that the degradation is not a constant but increases as the octane number of the distillate is increased. Higher yields of a given octane-number product are obtained at

TABLE 43.—OCTANE NUMBER AND YIELD

Stock	A.P.I.	Approximate degradation	Type of operation
Straight-run naphtha	51	0.37	Coil only or coil and soaker—once through
Cracked naphtha	45	0.68	Once through
Cracked naphtha	45	1.3	Currently recycling

higher pressures. By their tests, an increase of 10 per cent in the yield was obtained when the pressure was increased from 250 to 800 lb. per square inch. Yields of total distillate are seldom more than 80 per cent, which means a gas loss of 20 per cent.

Example 54. Octane Number of Gasoline by Reforming.—A straight-run naphtha has an octane-number of 35. If it is cracked in a once-through cracking equipment for the production of 80 per cent total distillate, what will be the octane number of the distillate?

$$\text{Total change in percentage} = (100 - 80) = 20$$

Each decrease of 0.37 per cent causes an increase of 1 in the octane number (Table 43).

$$\text{Octane number of distillate} = \frac{20}{0.37} + 35 = 89$$

The octane number of a 90 per cent yield would be lower:

$$\text{Octane number} = \frac{(100 - 90)}{0.37} + 35 = 62$$

These experimenters[10] fail to report the exact operating conditions for each test, and hence the changes in octane number that they report may be due, in part, to differences in the temperatures or operating conditions, as well as to differences in the yield. In fact Egloff and Nelson[11] show no change in octane number with different yields if the operating conditions are kept the same in each test. When Smackover fuel oil is cracked, the yield is increased from 39 to 63 per cent by cracking more and more completely, but the octane number of the pressure distillate remained the same. Egloff's[11] tests are not comparable with those of LeRoi[10] because different equipments and conditions were used and particularly because Egloff reported the octane number of the gasoline and LeRoi reported the octane number of the total product.

Albright[12] shows that an increase in temperature increases the octane number of the gasoline, if other conditions are kept the same. The octane number was increased from 69 to 72 by increasing the temperature in a commercial unit from 997 to 1010°F.

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[11] Cracking Light and Heavy Oils, 3d Midyear Meeting, A.P.I., Tulsa, Okla., May, 1933.

[12] Influence of Temperature in Reforming Naphtha, *Ref. Nat. Gaso. Mfr.*, January, 1933, p. 2.

Turner and LeRoi[13] find that the octane number of reformed naphtha can be computed as a function of the equivalent time at 900°F.

The octane number of a cracked gasoline can be estimated with fair accuracy from the A.S.T.M. distillation and A.P.I. gravity.[14] Equations are

$$\text{Octane number (high)} = 82.8 - 65\,(4 \log \text{A.P.I.} + 2 \log 10\% + 1.3 \log 90\% - 14.46) \quad (46)$$

$$\text{Octane number (low)} = 71.0 - 132\,(3.5 \log \text{A.P.I.} + 1.25 \log 10\% + 1.6 \log 90\% - 12.92) \quad (47)$$

TABLE 44.—YIELD AND OCTANE NUMBER

Stock	Source	A.P.I.	Yield gaso.	Temp., deg. F.	Pressure, lb. per sq. in.	Octane number	
						Stock	Gasoline
Gasoline...........	Pa.	64.6	76.7	1000	400	50	75
Gasoline...........	Joiner and E. Tex.	58.7	84.4	950	500	56	75
Gasoline...........	Joiner and E. Tex.	58.7	88.1	950	500	56	71
Gasoline...........	E. and W. Tex.	61.3	85.8	995	450	59	73
Gasoline...........	M.C.	59.8	82.3	975	500	42	70
Gasoline...........	West Tex.	58.1	87.4	950	750	61	78
Naphtha..........	Pa.	54.9	73.5	950	500	31	76
Naphtha..........	M.C.	53.5	75.5	1000	500	34	75
Naphtha..........	West Tex.	51.5	80.4	950	750	52	78
Gas oil............	Pa.	38.8	70.5	950	350	..	76
Gas oil............	M.C.	35.3	65.2	965	350	..	80
Gas oil............	Calif.	34.5	70.8	950	350	..	77
Gas oil............	East Tex.	32.0	60.5	950	350	..	75
Gas oil............	Coastal	28.5	52.8	950	400	..	90
Gas oil............	Calif.	26.1	55.6	950	350	..	79
Fuel oil...........	New Mex.	27.8	56.0	935	350	..	76
Fuel oil...........	Mont.	27.3	60.2	950	300	..	81
Fuel oil...........	M.C.	25.3	51.2	915	250	..	72
Fuel oil...........	Ky.	23.4	55.1	900	265	..	76
Fuel oil...........	Calif. S. F. Spgs.	19.8	40.7	929	250	..	75
Fuel oil...........	Calif.	17.8	38.9	890	250	..	79
Fuel oil...........	Smackover, Ark.	17.9	48.8	935	200	..	80

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[13] Octane-number Improvement in Naphtha Reforming, *Ind. Eng. Chem.*, **27**, 1347 (1935).

[14] Cox, R. B., Gasoline Octane Rating, *Ref. Nat. Gaso. Mfr.*, February, 1940, p. 31.

Note that logarithms to the base 10 are employed. Octane numbers from 15 to 70 are classed as low octane numbers and from 62 to 83 as high octane numbers.

Reference 11 also constitutes a good résumé of the octane number that may be expected when operating with various stocks and at different operating conditions. The data given in Table 44 were taken from this paper.[11] The Dubbs process was used.

Heat of Decomposition.—Little definite information can be given regarding the heat that is required for the cracking reaction. Theoretical methods of computing the heat of decomposition—and several of these are available—all fail because the data required to apply them are not usually available. Nevertheless, all of these methods indicate clearly that if large amounts of gas are produced, the heat of decomposition is relatively high and, if a process could be operated so that no gas was produced, the cracking reaction would generate rather than require the addition of heat.[15] These methods also show that the heat of decomposition for heavy fuel oils is higher than for gas oil or naphtha stocks.

The magnitude of the heat of decomposition expressed as B.t.u. per pound of 437°F. gasoline that is produced is indicated in Table 45. The heat of decomposition applies to a reaction in which a liquid is decomposed into both gaseous and liquid products, and hence the latent heat of vaporization is contained in the heat of decomposition and does not need to be included in heat-balances.

Perhaps the most reliable method of computing the heat of decomposition is by means of the first law of thermodynamics as outlined in Examples 30 and 31 (Chap. XII). The heat of combustion is an accurate measure of the chemical energy content of a material. Hence the difference between the heat of combustion of the cracking-stock and the total heat of combustion of the products of cracking is the heat required for cracking. Heats of combustion are normally given at 60°F., and hence it is necessary either to convert all of these to the cracking temperature or to convert the computed heat of decomposition at 60°F. to the cracking temperature. Example 55 illustrates the application of this method.

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[15] Perhaps this accounts for the rise in temperature that sometimes occurs as an oil flows slowly through a soaking drum. This phenomenon has been frequently reported by plant operators.

TABLE 45.—HEAT OF DECOMPOSITION

Reference	B.t.u. per lb. gaso.	Method of determination
Leslie and Potthoff[16].	900	Laboratory measurements
Obrayachikov and Velikanov[17]	630	3 commercial heat-balances
Weir and Eaton[18] (0–24% gaso.).....	808*	31 laboratory tests
Weir and Eaton (24% gaso. up)....	429	7 laboratory tests
Author.............	671	6 commercial heat balances
Author.............	1920†	Computed for $C_2H_6 \rightarrow C_2H_4 + H_2$
Author.............	1309†	Computed for $C_3H_8 \rightarrow C_3H_6 + H_2$
Author.............	659†	Computed for $C_3H_8 \rightarrow C_2H_4 + CH_4$
Author.............	993†	Computed for $nC_4H_{10} \rightarrow C_4H_8 + H_2$
Author.............	528†	Computed for $nC_4H_{10} \rightarrow C_2H_4 + C_2H_6$
Author.............	546†	Computed for $nC_4H_{10} \rightarrow C_3H_6 + CH_4$

* 410°F. A.S.T.M. end-point.

† B.t.u. per pound of feed material.

Example 55. Computation of Heat of Decomposition.—One hundred pounds of a gas oil and recycle cracking-stock is cracked to produce 17.1 lb. of fixed gas, 57.5 lb. of pressure distillate, and 25.4 lb. of cracked tar. What is the heat of decomposition at 60 and at 900°F.?

Basis: 100 lb. cracking-stock. A negative sign means heat liberated.

Heats of combustion at 60°F.:

	B.t.u. per Lb.
Cracking-stock..................................	19,370
Fixed gas..................................	21,200
Pressure distillate..................................	20,200
Cracked tar..................................	18,100

These may be estimated by the data given in Chap. VIII.

Energy available in stock:

Heat in cracking-stock 100(−19,370) −1,937,000 B.t.u

Energy available in products:

Heat in gas.....	17.1(−21,200) =	− 362,000	
Heat in P.D....	57.5(−20,200) =	−1,160,000	
Heat in tar....	25.4(−18,100) =	− 460,000	
Subtracting.....................		−1,982,000	−1,982,000
Difference in energy..........	Heat absorbed =		+ 45,000

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[16] *Ind. Eng. Chem.*, **18**, 776 (1926).

[17] *Neftyanoe Khozyaistvo*, **17**, 370 (1929); and *C. A.*, **24**, 1206 (1930).

[18] *Ind. Eng. Chem.*, **29**, 346 (1937).

Heat of decomposition B.t.u. per pound of gasoline at 60°F. $= \frac{45{,}000}{57.5} = 782$

Heat of decomposition at 900°F. (the sensible heat contents were computed from Figs. 33 and 34):

Cool stock from 900 to 60°F...	100(−580)		= − 58,000
Decomposition at 60°F........		= + 45,000	
Heat gas to 900°.............	17.1(655)	= + 11,200	
Heat P.D. to 900°............	57.5(642)	= + 36,900	
Heat tar to 900°.............	25.4(492)	= + 12,650	
		+105,750	+105,750
Difference in energy.........	Heat absorbed (adding)		= + 47,750

$$\text{Heat of decomposition, B.t.u. per pound at 900} = \frac{47{,}750}{57.5} = 830$$

Although the method outlined in Example 55 is correct from the standpoint of theory, it is hardly satisfactory for practical work unless great care is used. Very small errors in the heats of combustion or in the yields of products that are assumed will introduce great errors in the computed heat of decomposition. However, many useful generalizations can be determined. As an example, Obrayachikov[19] has computed the following tabulation. The first column is the yield of gasoline in a single cracking operation (or the crack-per-pass), and the second column shows the heat required to produce a pound of gasoline.

Yield	Heat of Decomposition per Lb. Gasoline, B.t.u.
5	2,700
10	1,710
15	1,170
20	900
25	865
35	790

The results shown in this tabulation might be expected, inasmuch as a large amount of energy is used to produce recycle stock when only a small amount of gasoline is produced but relatively less heat is used to make recycle stock when the yield of gasoline is greater.

Yields by Cracking.—The estimation of the yields that may be expected when cracking a particular stock is always a troublesome problem. These may be obtained by laboratory cracking operations, but such yields are often worthless because the laboratory procedure does not duplicate plant operation. In the past the yields have been estimated by referring to scattered data from plant operations, but to the author's knowledge no comprehensive organization of these plant data has been made.

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[19] *Ref. Nat. Gaso. Mfr.*, January, 1932, p. 34.

The over-all reaction of cracking involves the decomposition of a heavy oil into gas, low-boiling oils, and tar. In this operation the hydrogen in the stock is concentrated into the light products, and hence the residue material becomes more and more deficient in hydrogen. Thus the larger the percentage of distillate produced the higher will be the specific gravity of the residue that is left behind. The yield of gasoline is directly related to the difference in gravity of the stock and the gravity of the tar. Approximate yields by cracking are

$$Y_{cr} = 30.8 + 0.035(S - T)\frac{D}{C} \tag{48}$$

$$Y_{fo} = 303 - 250d \tag{49}$$

$$Y_{go} = 331 - 300d \tag{50}$$

$$G = 0.45(S - T) \tag{51}$$

where Y_{cr} = per cent gasoline by cracking gas oil or fuel oil.
Y_{go} = per cent 400 E.P. gasoline by coking gas oil.
Y_{fo} = per cent 400 E.P. gasoline by coking fuel oil.
G = per cent unaccounted-for losses.
S = A.P.I. gravity of charging-stock.
T = A.P.I. gravity of cracked fuel oil.
d = specific gravity of stock being coked.
D = end-point of gasoline.
C = characterization factor.

Great accuracy cannot be claimed for the equations. The computed yields are seldom in error over ±5 per cent, but a few data indicate larger losses. The equations should not be applied to abnormal cracking operations such as the production of very low gravity tars (3 A.P.I.) or for very mild cracking ($S - T$ equals only 5). Reforming operations cannot be correlated by simple equations of these types. An indication of the accuracy of Eq. (51) is given in Table 46.

Thus larger losses occur when gas oil is cracked than for fuel oil. This may be explained by the fact that gas oil must be heated to a higher temperature or for a longer time than fuel oil to produce the same yield of gasoline.

TABLE 46.—GAS AND UNACCOUNTED-FOR LOSSES

Difference in sp. gr. of stock and tar	Per cent gas and unaccounted-for losses		
	Gas oil	Fuel oil	An average by Eq. (51)
0.05	7	4	4
0.10	9	6.5	7
0.15	11.7	10.0	11
0.20	15.5	12.0	14.2

A comparison of the yield in the coking of gas oil and of fuel oil also reveals the more refractive nature of gas oil. For the same gravity of stock, the yield from fuel oil is greater than from gas oil. With reference to Eqs. (49) and (50), the yields when 0.9 specific gravity (25.8 A.P.I.) stocks are coked are

$$\text{Yield from fuel oil} = 303 - 250 \times 0.9 = 78 \text{ per cent}$$
$$\text{Yield from gas oil} = 331 - 300 \times 0.9 = 61 \text{ per cent}$$

In applying the foregoing formulae it is necessary to rely upon experience in estimating what A.P.I. of tar is possible. If the tar has too low a gravity, it may be so viscous that it cannot be easily withdrawn from the cracking unit or it may not be marketable. Straight-run tars are viscous, but cracked tars are much more fluid. When distilled stocks are cracked, tars having gravities from 3 to 7 A.P.I. are usually fluid enough to be marketable. The tars obtained by cracking all of a fuel oil are more viscous, and A.P.I. gravities of 6 to 9 are advisable. In some plants it is the practice to distill gas oil from fuel oil and leave a partially cracked straight-run tar behind. Thus the tar from many cracking plants consists of a mixture of straight-run and cracked tars. These mixed tars are even more viscous and gravities of 8 to 11 are necessary. In reforming operations, cracked tars having gravities of 3 to 5 A.P.I. are common. An idea of the viscosity of cracked and Mid-Continent straight-run tars (or fuel oils) may be gained from the following tabulation:

A.P.I.	Furol viscosity at 122°F.	
	Pure cracked	Straight-run
2.5	1000	
5.0	150	
7.5	20	
17.5	....	700
20.0	....	200
25.0	....	16

In general, the yield of gasoline is increased by the following conditions:

1. A low crack-per-pass or a high recycle ratio.
2. A relatively low pressure (200 to 300 lb.).
3. A relatively low cracking temperature (860 to 900°F.).
4. The cracking of all of a black or residual stock rather than the production of a distilled cracking-stock and a residue of heavy tar. At the same time a black stock tends to produce coke in the tubes.
5. A low octane-number gasoline.

Example 56. Yields by Cracking.—A 24 A.P.I. Mid-Continent fuel oil is to be cracked to produce 400 end-point gasoline and an 8 A.P.I. tar. What approximate yields may be expected?

Yield gasoline [Eq. (48)] $= 30.8 + 0.035(24 - 8)\frac{400}{11.8} = 49.8$ per cent
Unaccounted for loss [Eq. (51)] $= 0.45(24 - 8) = 7.2$ per cent
Cracked fuel oil (by difference) $= 43.0$ per cent

These are ultimate yields. In determining the yield of pressure distillate, approximations must suffice. The loss during the rerunning of pressure distillate usually amounts to about 2 per cent, although the magnitude of the loss is determined by the character of the distillate and type of treatment. The bottoms obtained in the rerunning of the treated pressure distillate is often blended with the cracked tar. The viscosity of the tar is sometimes high, and the addition of even a small amount of pressure distillate butts serves to lower the viscosity a large amount.

If a 440 end-point distillate is produced, the approximate yield would be

$$\text{Yield of P.D.} = 30.8 + 0.035(24 - 8)\frac{440}{11.8} \quad 51.7 \text{ per cent}$$

The approximate yields of gasoline when operating in other ways would be

When making a 10 A.P.I. fuel oil, $30.8 + 0.035(14)\frac{400}{11.8} = 47.4$ per cent
If coking, $303 - 250 \times 0.91 = 75.0$ per cent

Yields from Hydrocarbons.—In the thermal decomposition of butane and iso-butane, the principle reactions are as follows:

$$nC_4H_{10} \rightleftarrows nC_4H_8 + H_2 \qquad (52)$$
$$nC_4H_{10} \rightarrow C_3H_6 + CH_4 \qquad (53)$$
$$nC_4H_{10} \rightarrow C_2H_4 + C_2H_6 \qquad (54)$$
$$2nC_4H_{10} \rightarrow nC_4H_8 + C_3H_8 + CH_4 \qquad (55)$$
$$2nC_4H_{10} \rightarrow nC_4H_8 + 2C_2H_6 \qquad (56)$$
$$iC_4H_{10} \rightleftarrows iC_4H_8 + H_2 \qquad (57)$$
$$iC_4H_{10} \rightarrow C_3H_6 + CH_4 \qquad (58)$$
$$iC_4H_{10} \rightarrow C_2H_4 + C_2H_6 \qquad (59)$$
$$2iC_4H_{10} \rightarrow iC_4H_8 + C_3H_8 + CH_4 \qquad (60)$$

The reversible equations (52) and (57) are suppressed by pressure, but the bimolecular reactions, Eqs. (55) and (60), are promoted by pressure. The equilibrium constants for dehydrogenation reactions have been summarized by Grosse and Ipatieff.[20]

The extent to which each of the various reactions takes place is dependent upon the pressure and temperature; but since commercial practice is limited to high pressures in order to keep gas volumes low and to high temperatures in order to hasten the rate of reaction, only the high-pressure data of Tropsch, Thomas, and Egloff[21] will be given here. Average equations of their data[21] at about 1020°F. and at 725 lb. per square inch pressure are

$$100nC_4H_{10} \rightarrow 19.25C_4H_8 + 33C_3H_6 + 30C_2H_4 + 16C_3H_8 + 33.5C_2H_6 + 49CH_4 + 1.5H_2 \qquad (61)$$
$$100iC_4H_{10} \rightarrow 29iC_4H_8 + 43C_3H_6 + 5.5C_2H_4 + 22.5C_3H_8 + 5.5C_2H_6 + 65.5CH_4 + 6.5H_2 \qquad (62)$$

Similar data have been published by various investigators;[22,23,24] and although the exact products that are produced at various pressures and temperatures vary somewhat, the total production of olefins from either normal or isobutane and the total volume of gaseous products are remarkably uniform:

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[20] Catalytic Dehydrogenation of Gaseous Paraffins, *Ind. Eng. Chem.*, **32**, 268 (1940).

[21] Pressure Pyrolysis of Gaseous Paraffin Hydrocarbons, *Ind. Eng. Chem.*, **28**, 324 (1936).

[22] EGLOFF, THOMAS, and LINN, Pyrolysis of Propane and the Butanes, *Ind. Eng. Chem.*, **28**, 1283 (1936).

[23] ECHOLS and PEASE, Kinetics of the Decomposition of *n*-Butane, *J. Am. Chem. Soc.*, **61**, 208 (1939).

[24] NEUHAUS and MAREK, Thermal Decomposition of *n*-Butane into Primary Products, *Ind. Eng. Chem.*, **24**, 400 (1932).

Mols of olefins produced = 80–85 per cent of mols of butanes
Total mols of products = 190 per cent of mols of butanes

Such yields cannot be obtained commercially unless recycling is used, because polymerization consumes part of the yield. In general, short reaction times, a low crack-per-pass, low pressures, and high temperatures are the best operating conditions, but each of these is limited by economics or practical considerations in commercial practice. Long times or a low crack-per-pass require large equipment; low pressures require the handling of large amounts of vapor; and temperatures are limited by the alloy materials that are available for tubes.

(Reference 25) Cracking time: 12 min.
Cracking temperature: 842°F.

Stock	Sp. gr.	392°F. distillate per cent by weight	Reaction* vel. constant
Kerosene	.....	4.9	0.0000672
Solar oil	.....	18.6	0.000288
Paraffin oil	0.833	26–30	0.000457
Spindle oil	0.904	28.2	0.000461
Three cylinder oils	0.931	29.5–30.5	0.000498
Paraffin	.....	31.2	0.000518

* Computed by author by Eq. (63).

(Reference 21) Cracking time: 64 min.
Cracking temperature: 796°F.

Stock	Boiling-range, deg. F.	Sp. gr.	392°F. distillate per cent by weight	Reaction* vel. constant
Kerosene	428–518	0.81	14.9	0.0000415
Gas oil	518–572	0.834	15.8	0.0000443
Solar oil	572–617	0.859	17.6	0.0000505
Engine oil	....	0.91	22.4	0.0000660

* Computed by author from Eq. (63).

Rate of Cracking.—The rate at which cracking occurs is governed mainly by three factors: the temperature, the time, and the character of the cracking-stock. The yield in a given length of time increases rapidly with temperature; the yield at a fixed temperature increases with time up to a certain point, and then it decreases; and the yield for a given length of time is greater for heavy stocks. The tabulations shown on page 304, which were taken from the work of Sachanen and Tilicheyev,[25,26] indicate the relation of the rate of cracking to the properties of the cracking-stock.

Thus the lighter the cracking-stock the longer the time required. In commercial practice the yield from light stocks is obtained not by using a long length of time but by using a higher temperature. As will be shown later, an increase in temperature is very effective in decreasing the time required. Stocks that have already been cracked, such as recycle stock, also require a longer time. In general, stocks that require a relatively long time for a given yield are termed *refractory stocks.* Recycle stock, kerosene, naphtha, and gasoline are classed as refractory stocks.

The cracking reaction may be described in a general way as a first-order reaction if the decomposition is limited to a low conversion-per-pass (20 to 25 per cent):

$$K_1 = \frac{1}{t} \ln \frac{a}{a - x}; \text{ or often, } = \frac{1}{t} \ln \frac{100}{100 - x} \qquad (63)$$

where K_1 = reaction velocity constant (Fig. 94).
t = time, sec.
a = percentage of material in feed-stock—for a pure feed-stock $a = 100$.
x = percentage of material that disappears during the reaction time t.

In order to use the equation in designing cracking equipment it is necessary to assume that x represents the percentage of product that is produced. Several different definitions of the term x are used on Fig. 94:

1. Hydrocarbons (methane through heptane). The term x is used as mol (or gas volume) percentage, and it refers to the disappearance of the feed-stock hydrocarbon.

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[25] *Oil Gas J.*, June 23, 1927, p. 144.

[26] *J. Inst. Petroleum Tech.*, **14**, 761 (1928).

2. Cracking stocks (naphtha through residuums). The term x is used as liquid-volume percentage of 400 E.P. gasoline that is produced.

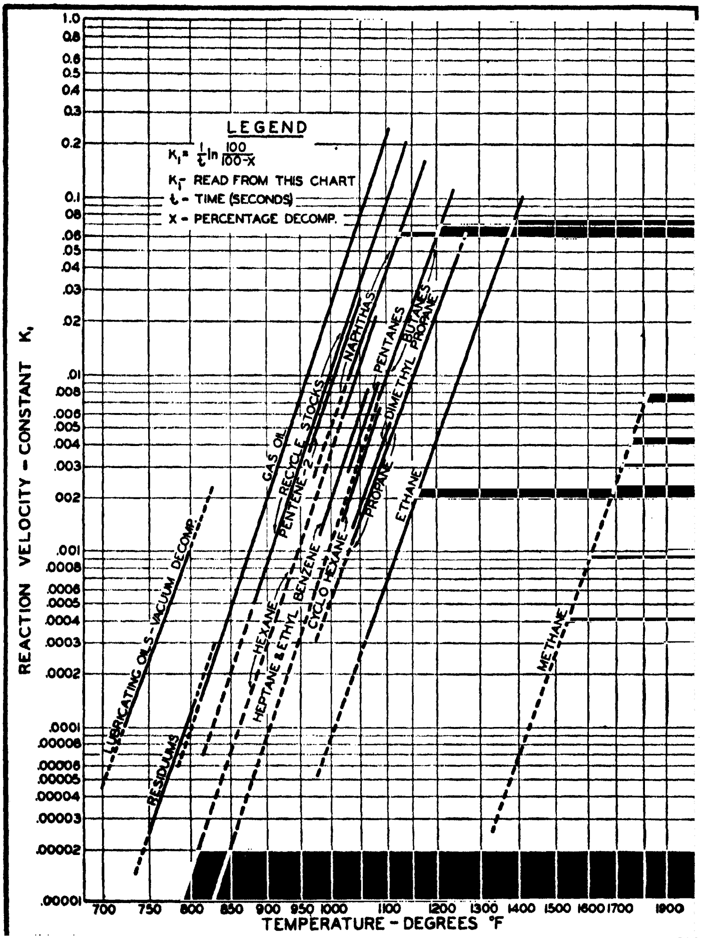

Fig. 94.—Reaction velocity constants for the decomposition of hydrocarbons and petroleum fractions. (*Courtesy of Oil Gas J.*)

3. Lubricating oils (by vacuum decomposition). The term x is used as liquid-volume percentage of lubricating oil that is produced. A slight error results because the rate differs some-

what depending upon the viscosity of the lubricating oils that are produced.

The exact types of reactions that are contemplated in using Fig. 94 or the kinds of products that will be produced must be gained from independent sources or reference to the original data[27] used in plotting Fig. 94. The constants may be used for either liquid- or vapor-phase reactions.

The reaction velocity constant may be related to temperature by the following form of equation:

$$\ln K_1 = \frac{-E}{RT} + C$$

where R = gas law constant = 1.985.
T = absolute temperature, deg. K.
E = energy of activation, cal.
C = a constant.

For gas oil the value of E is about 55,000 and of C is about 30.

Effect of Time.—In general, the longer the length of time the greater the yield. However, the yield decreases if the time is very long. This is illustrated by the data of Watermann and Perquin[28] (Fig. 95) for paraffin wax. As cracking starts, primary decomposition reactions take place; but as the time is increased, the concentration of reactive unsaturated materials increases and polymerization reactions begin to be important. These combination reactions use some of the material that has been formed by decomposition so that the yield of gasoline decreases. In Fig. 95 the curve of the cracking rate is nearly linear out to 30 per cent. This shows that only one factor, *viz.,* decomposition, is greatly affecting the yield. But at 30 per cent the effect of polymerization becomes marked; and at 48 per cent the rate at which polymerization is taking place is more rapid than the rate of decomposition, and the yield becomes less. As the yield becomes less, large amounts of tar are produced and coke may be formed. Hence commercial processes are never operated at times that are greater than the time at the maximum point in the time-yield curve. If recycling is practiced, the conversion-per-pass must be well below the maximum point, but for once-through operation the conversion-per-pass may approach the maximum point closely.

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[27] Data for Fig. 94: BRAGG, L. E., *Ind. Eng. Chem.*, **33**, 376 (1941); HAGUE and WHEELER, *J. Chem. Soc.*, pp. 378–393 (1929); BONE and COWARD, *J. Chem. Soc.*, pp. 93–94, 1197 (1908); MAREK and MCCLUER, *Ind. Eng. Chem.*, **23**, 878 (1931); FREY and HEPP, *Ind. Eng. Chem.*, **24**, 282 (1932); PEASE and DURGAN, *J. Am. Chem. Soc.*, **52**, 1262 (1930); HURD and SPENCE, *J. Am. Chem. Soc.*, **51**, 3353 (1929); TROPSCH, THOMAS, and EGLOFF, *Ind. Eng. Chem.*, **28**, 324 (1936); EGLOFF, THOMAS, and LINN, *Ind. Eng. Chem.*, **28**, 1283 (1936); GENIESSE and REUTER, *Ind. Eng. Chem.*, **24**, 219 (1932); KEITH, WARD, and RUBIN, *Proc. A.P.I.*, 1933; PEASE and MORTON, *J. Am. Chem. Soc.*, **55**, 3190 (1933); FREY and HEPP, *Ind. Eng. Chem.*, **25**, 441 (1933); MAREK and NEUHAUS, *Ind. Eng. Chem.*, **25**, 516 (1933); FREY, *Ind. Eng. Chem.*, **26**, 198 (1934); PAUL and MAREK, *Ind. Eng. Chem.*, **26**, 454 (1934); MEID and BURKE, *Ind. Eng. Chem.*, **27**, 299 (1935); older references used in drawing Fig. 95 in "Petroleum Refinery Engineering," 1st ed., pp. 322–323, 329; and laboratory tests by the author on viscosity breaking and vacuum decomposition.

[28] *J. Inst. Petroleum Tech.*, **11**, 36 (1925).

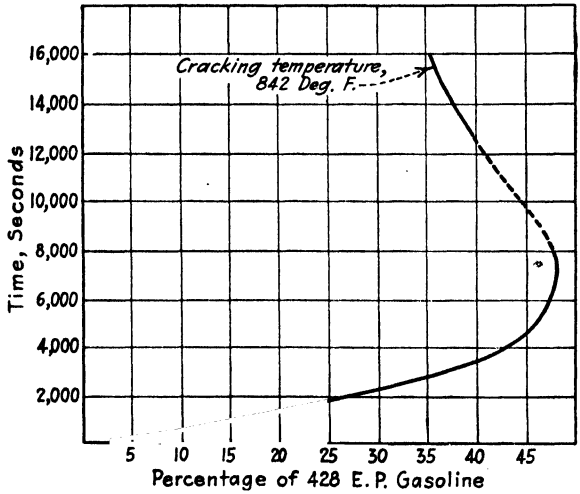

FIG. 95.—Yield of gasoline versus time at 842°F. (*Watermann and Perquin, J. Inst. Petroleum Tech.*)

Temperature affects the general shape of the time-yield curve. The maximum percentage point is lower for high cracking temperatures and also lower for stocks that have already been cracked. Thus at high temperatures the rate of polymerization is relatively faster than at low temperatures. The maximum points and times for several sets of data are shown in Table 47.

The use of reaction chambers and soaking drums is to some extent being abandoned, except when coke is desired, because of the decreased yields at a long length of time. However, in some modern plants, the use of reaction chambers for soaking the vapor has resulted in both increased capacity and an increased yield. The maximum points are also the governing factor in determining the recycle ratio that is possible.

TABLE 47.—TIME FOR MAXIMUM YIELD OF GASOLINE

Temperature, deg. F.	Max. yield in a single operation	Time, sec. at max. yield	Phase	Stock	Reference
700	Negative*	20,000+	Liquid	Recycle oil	29
800	40	14,000	Liquid	Gas oil	30
842	48†	7,500	Liquid	Paraffin wax	28
932	31	1,000	Vapor	Gas oil	31
1,076	26	30	Vapor	Gas oil	31
1,184	23	3	Vapor	Gas oil	31

* Yield decreases with time, probably owing to recycle stock.

† Either poor data or the stock, paraffin wax, caused the maximum point to be high.

An idea of the lengths of time used in commercial processing may be gained from the following tabulation:

Operation	Time, Sec.
Butane decomposition at 1000°F	380
Reforming (once through) at 1000°F	300
Cracking (mixed phase recycling) at 900°F	170
Viscosity breaking (once through) at 860°F	150
Reforming (recycling) at 980°F	130
Butane decomposition at 1100°F	40
Cracking (vapor-phase recycling) at 1050°F	3
Cracking (vapor-phase recycling) at 1150°F	0.3

Recycle stocks require more time for a given yield than straight-run stocks. The following tabulation indicates the refractive nature of these stocks. The figures refer to the ratio of the yield from recycle stock to the yield from fresh stock, if the two are cracked under the same conditions of time, temperature, and pressure.

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[29] LESLIE and POTTHOFF, *Ind. Eng. Chem.*, **18**, 776 (1926).

[30] CROSS, "Handbook of Petroleum, Asphalt, and Natural Gas," *Bull.* 25, p. 287, 1928.

[31] GENIESSE and REUTER, *Ind. Eng. Chem.*, **24**, 219 (1932).

Once cracked	Twice cracked	Current recycling	Thrice cracked	Reference
0.6	0.318	....	0.175	7
0.79	.....	....	.....	7
0.795	0.69	....	.....	8
.....	.....	0.4–0.47	.....	16
.....	.....	0.43	.....	Fig. 94

Recycle stock, regardless of recycle ratio, will consist almost entirely of material that has been cracked once and twice. Hence the currently recycled stock will crack about half as readily as fresh stock.

Recycling in Cracking Plants.—In commercial plants the ultimate yield of pressure distillate is not produced in a single cracking operation. Recycle stock and gas oil are charged to the cracking heater, and a relatively small percentage yield from this large amount of mixed stock is a large yield when based on the original stock. As an example, assume that two parts of recycle and one part of fresh stock are cracked giving a yield, based on the mixture, of 20 per cent, or $0.2 \times 3 = 0.6$ parts of distillate. Based on the one part of fresh stock, which is all that comes into the plant, the yield of pressure distillate is $0.6 \times 100 \div 1 = 60$ per cent.

Recycling is necessary because coke is deposited and a large gas loss occurs if high yields per pass are produced. The tarry material and the reactive materials that are produced during cracking seem to be the source of coke. If the yield is great, the maximum point shown in Fig. 95 is approached, and polymerization takes place with the formation of tar and coke. These products are always produced to some extent, but in the recycling operation they are currently eliminated. The common arrangement is to cycle the cracked material that issues from the pipestill, through a fractionating system. In the fractionating system the tarry materials are eliminated into the pressure-still tar; the gas and pressure-still distillate pass overhead; and a heart-cut material consisting of fresh gas oil and recycle is withdrawn as a clean distillate which is continuously pumped into the pipestill. Thus the same quantity of recycle stock and of fresh gas oil or reduced crude oil is charged to the pipestill each hour, and constant quantities of recycle, gas, distillate, and cracked tar issue from the outlet of the still each hour.

The relative quantities handled at various points in a particular type of cracking system are illustrated in Fig. 96. The quantities in the figure are given in barrels and are based on a charge of 100 bbl. of a fuel oil charging-stock. The charging-stock consists of 85 bbl. of gas oil and 15 bbl. of straight-run tar. The charge is heated by exchangers and a heater, if necessary, and is then mixed with the hot cracked material that issues from the pipestill. In evaporator *A* everything except the straight-run tar and the cracked tar is vaporized. In the fractionator *B* the pressure distillate and gas are eliminated, and the gas oil and recycle stock are separated and returned to the pipestill.

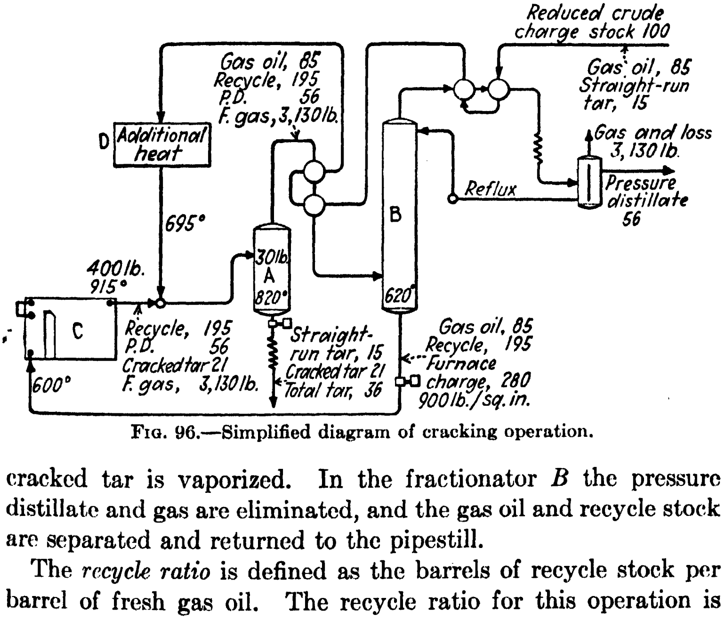

FIG. 96.—Simplified diagram of cracking operation.

The *recycle ratio* is defined as the barrels of recycle stock per barrel of fresh gas oil. The recycle ratio for this operation is 195/85, or 2.3, and the *crack-per-pass* is 56/280, or 20 per cent. The recycle ratio is sometimes used as the barrels of recycle divided by the plant charge (100 bbl. in this case). Such a definition of recycle ratio is not logical in the system illustrated because the entire 100 bbl. is not exposed to cracking conditions.

The general effect of increasing the crack- or conversion-per-pass is as follows:

1. Lower gasoline yield.
2. Higher octane number.

3. An increased tendency to produce coke.
4. The production of more gas.
5. An increase in the volatility of the light-end of the gasoline.

In most respects it is an advantage to use a low crack-per-pass, or a high recycle ratio, but the cost of the plant is much greater.

If the percentage of distillate that is produced per pass is high, coke will be deposited in the tubes and the entire operation may be prematurely terminated. Commercial operating data show that the allowable crack-per-pass for liquid-phase processes is between 13 and 20 per cent and for vapor-phase processes 8 and 13 per cent. The crack-per-pass is definitely related to the maximum points shown in Table 47. The allowable crack-per-pass for recycling processing is about half of the maximum yield of gasoline that can be produced in a single cracking operation. Thus the allowable crack-per-pass for a liquid-phase process operating at 800°F. (Table 47) is about 40/2, or 20 per cent, and for a vapor-phase process operating at 1184°F. about 11 per cent. For once-through processing systems the crack-per-pass may be larger. The reason for the relation between the crack-per-pass and the maximum yield is the fact that the fresh stock is cracked much more severely than the recycle stock. Both stocks are in the cracking zone for the same length of time, but the yield from the recycle stock is only about half as large as the yield from the gas oil. Thus the gas oil is being cracked at a yield that is close to the maximum point, but the recycle stock is being cracked for a yield that is less than the average crack-per-pass (Example 58). At very high cracks-per-pass the gas oil will be cracked for a time greater than that for the maximum yield, and coke will be formed.

Example 57. Material Balance and Crack-per-pass.—A cracking plant is to operate at a cracking temperature of 915°F. and at 400 lb. per sq. in. Assume that 80 per cent 27.5 A.P.I. gas oil can be distilled from the fuel oil. Make material balances to show the quantities of the stocks at all points. What recycle ratio and crack-per-pass should be used?

Basis: 100 gal. of fuel oil charging-stock.

Ultimate yields are

	Per Cent
Pressure distillate (440 E.P.)	54
Gas and loss	6.1
Fuel oil	39.9

MATERIAL BALANCE OF FUEL OIL CHARGING-STOCK

Material	Per cent or gal.	A.P.I.	Lb. per gal.	Total lb.
Fuel oil, charging-stock . . .	100	24	7.58	758
Gas oil.	80	27.5	7.41	593
Straight-run tar.	20	. . . .	. . . .	165

Lb. of straight-run tar 758 − 593 = 165
Lb. per gal. of tar $^{165}\!/_{20}$ = 8.25

The A.P.I. corresponding to 8.25 lb. per gal. is 11.3.

MATERIAL BALANCE OF PLANT TAR

Plant tar	Per cent or gal.	A.P.I.	Lb. per gal.	Total lb.
Total tar.	39.9	8.0	8.45	337
Straight-run tar.	20	11.3	8.25	165
Cracked tar.	19.9	. . . .	. . . .	172

$$\text{Lb. per gal. of cracked tar } \frac{172}{19.9} = 8.64$$

A.P.I. of cracked tar is about 4.8.

Recycle ratio:

When cracking at 915°F. the allowable crack-per-pass is about 34 divided by 2 (Table 47), or 17 per cent. In general, a little higher value than this is possible, and hence 19 per cent will be used as the crack-per-pass. The total 54 gal. of distillate is 19 per cent of the charge to the furnace.

Furnace charge,

$$\frac{54}{0.19} = 284 \text{ gal.}$$

MATERIAL BALANCE OF FURNACE CHARGE

Material	Per cent or gal.	A.P.I.	Lb. per gal.	Total lb.
Gas oil.	80	27.5	7.41	593
Recycle.	204	15.0*	8.04	1,640
Furnace charge.	284	. . . .	. . . .	2,233

* The A.P.I. of the recycle stock will be a little over half as much as the A.P.I. of the gas oil, or about 15 A.P.I.

Lb. per gal. of furnace charge,

$$\frac{2{,}233}{284} = 7.86$$

A.P.I. is 18.4.
Recycle ratio,

$$^{204}\!/_{80} = 2.55 \text{ parts recycle per part gas oil}$$

MATERIAL LEAVING PIPESTILL

Material	Per cent or gal.	A.P.I.	Lb. per gal.	Total lb.
Pressure distillate*	54	55	6.32	342
Recycle	204	15	8.04	1,640
Cracked tar	19.9	4.8	8.45	172
Fixed gas (by difference)	.....	....	....	79
Furnace charge	284.0	18.4	7.86	2,233

* Assume A.P.I. of distillate is 55.

Recycling in Butane Plants.—The thermal decomposition of butane is practiced in essentially the same manner as cracking. Differences arise only because the feeds and products have different boiling-ranges from those encountered in cracking plants. The feed to the pipestill consists of butane feed-stock mixed with a recycle stock that consists primarily of butane but usually contains some propane. The propane (and excess butane) serves as a diluent in keeping the concentration of the products of decomposition to a low value just as recycle stock keeps the concentration of tar to a low value in a cracking plant. The conversion-per-pass ranges from 5 to 13 per cent in decomposition plants. The primary difference between the two processing schemes lies in the manner of recovering the products or in recovering the recycle stock. In the butane plant the product is separated as a liquid in the fractionating system (or subjected directly to some process such as polymerization for utilization of the olefins) and the excess butane and propane are separated from the gaseous product to be employed as a recycle stock. Thus, butane plants require fractionating equipment similar to those used in natural gasoline plants and gas recovery systems, whereas separation systems operating at about atmospheric pressure are suitable for cracking plants. The butane decomposition plant shown in Fig. 97 should be compared directly with the cracking system shown in Fig. 96.

The system shown in Fig. 97 is usually employed with other systems such as polymerization, alkylation, etc., and such processes are inferred in the dotted-line operations indicated in the center of the diagram. High temperatures and pressures are necessary in the decomposition zone in order to care for the relatively large volume that is occupied by gaslike materials such as butane. If thermal polymerization is the process contemplated in the center of the diagram, the whole flow diagram is the same as a cracking process except that a long time element is required in the polymerization zone whereas in cracking plants the polymerization of tars, etc., is avoided in every way possible and particularly by cutting the time to a minimum.

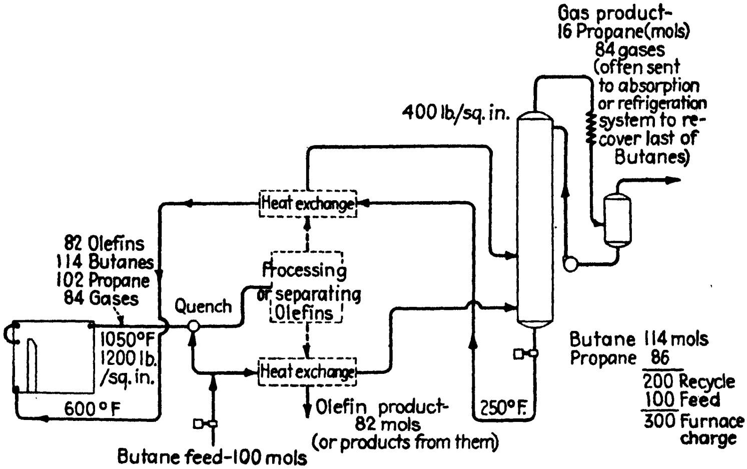

Fig. 97.—Typical thermal-decomposition system for butane (or hydrocarbons).

Effect of Temperature.—The temperature at which cracking starts to take place is between 680 and 700°F. This appears to be true even for decomposition at subatmospheric pressures (vacuum), although minor changes in color and viscosity appear at lower temperatures.

According to Fig. 94 and numerous investigators, the rate of thermal decomposition is found to increase rapidly with temperature. Various materials are affected differently by temperature, but variations are not great. The approximate number of degrees rise in temperature that will cause the rate of decomposition to double are

Decomposition temperature, deg. F.	Rate doubles for each—	Decomposition temperature, deg. F.	Rate doubles for each—
700	20.0°F.	1100	34.5°F.
800	22.0°F.	1200	39.0°F.
900	25.7°F.	1300	44.0°F.
1000	30.0°F.	1700	67.0°F.

The general relation among temperature, time, and yield is given by Eq. (63) and Fig. 94. It must always be recalled that these data do not apply to large yields or to situations in which polymerization (or secondary) reactions occur to such an extent that they undo the results of the primary decomposition reactions. For the usual situation, however, in which temperature varies, equations such as (66), and (64) and (65) must be employed.

Example 58. Temperature, Time, and Yield.—The cracking operation presented in Example 57 will be continued. Cracking is to occur at about 915°F.

How much time is required to give a crack-per-pass of 19 per cent? Basis: 284 gal. of furnace charge (or 100 gal. of reduced crude).

The recycle stock (204 gal.) will produce only 43 per cent as much gasoline as that which accrues from the fresh stock (gas oil). (Refer to page 310.)

Rate of cracking gas oil (let x = yield from gas oil):

$$\begin{aligned} 284(0.19) &= 80x + 0.43 \times 204x \\ x &= 32.2 \text{ per cent} \\ \text{Simultaneous yield from recycle} &= 13.85 \text{ per cent} \end{aligned}$$

At 915°F. the value of K_1 is 0.00296 (Fig. 94).

Time at 915°F. [Eq. (63)]:

$$t = \frac{1}{0.00296} \ln \frac{100}{100 - 32.2} = 337 \ln 1.452 = 126 \text{ sec.}$$

Note also that based on recycle stock, or on the mixture, the time is

$$t = \frac{1}{0.00122} \ln \frac{100}{100 - 13.85} = 820 \ln 1.16 = 122 \text{ sec.}$$

or

$$t = \frac{1}{0.0018} \ln \frac{100}{100 - 19} = 555 \ln 1.233 = 126.5 \text{ sec.}$$

For cracking at a constant length of time:

$$C_2 = C_0 2^{\left(\frac{T_2 - T_0}{x}\right)} \tag{64}$$

And for a constant yield,

$$V_2 = V_0 2^{\left(\frac{T_0 - T_2}{x}\right)} \quad \text{or} \quad = \frac{V_0}{2^{\left(\frac{T_2 - T_0}{x}\right)}} \tag{65}$$

where C_2 = yield for a given time at temperature T_2.
C_0 = yield for a given time at temperature T_0.
V_2 = time for a given yield at temperature T_2.
V_0 = time for a given yield at temperature T_0.
x = number of degrees required to double the yield.

An equation of the rate of cracking through a range of temperature can be derived as follows by assuming that the rate of heating is uniform. If the rate of heating appears to be far from uniform in some particular situation, the error can be reduced as much as deemed necessary by considering the heating range as a series of short temperature ranges.

$$C = C_0 2^{\left(\frac{T - T_0}{x}\right)}$$

where C = yield during heating for time t, per cent.
C_0 = yield, per cent per sec. at T_0.
T = final temperature, deg. F.
T_0 = initial temperature, deg. F.
x = a constant, average number of degrees to double yield.

If the heating takes place at a uniform rate,

$$T = T_0 + kt$$

where k = rate of heating, deg. F. per sec.
t = total time, sec.

$$C = \int_0^t dC = C_0 \int_0^t 2^{\left(\frac{kt + T_0 - T_0}{x}\right)} dt = C_0 \int_0^t 2^{\left(\frac{kt}{x}\right)} dt$$

$$C = C_0 \Big[\frac{1}{\ln 2} \cdot \frac{x}{k} \cdot 2^{\left(\frac{kt}{k}\right)} - \frac{1}{\ln 2} \cdot \frac{x}{k} \Big]_0^t$$

$$C = 1.44 \frac{C_0 x}{k} \left(2^{\left(\frac{kt}{x}\right)} - 1 \right) = 1.44 \frac{C_0 x}{k} \left(2^{\left(\frac{T - T_0}{x}\right)} - 1 \right) \tag{66}$$

Although cracking, in the normal sense, occurs at temperatures exceeding 680°F., other less vital changes take place when oils are heated to lower temperatures. These changes are most noticeable with lubricating oils. Many untreated lubricating oil stocks are discolored if they are heated even to 300°F. in the presence of air. If they are heated to higher temperatures for a long time, the viscosity and the gravity are also lowered. In the author's laboratory a paraffin-base lubricating oil was redistilled three times for the purpose of separating the oil into well-fractionated products of short boiling-range. During these distillations the temperature in the main body of liquid never exceeded 620°F. and the pressure was kept at less than 10 mm. The oil was heated for a total time of 22 hr. at 300 to 620°F. The viscosity and gravity dropped as follows:

30°F. fractions boiling at these average atmospheric boiling-points	Viscosity at 100°F.		Sp. gr.	
	Before	After	Before	After
700	57	56	0.8484	0.8471
800	104	99	0.8636	0.8616
900	245	229	0.8742	0.8729
1000	415	350	0.8825	0.8794

Effect of Pressure.—The technical literature offers many conclusions as to the effect of pressure on the cracking reaction, but most of these conclusions are based on experiments in which other variables, such as temperature or time, were not held constant. Such data are confusing because we cannot tell whether pressure or one of these other factors was the cause of the changes that occurred.

The most obvious effect of pressure is the fact that a high pressure suppresses vaporization and tends to produce a liquid-phase whereas a low pressure allows a vapor-phase to be produced. Obviously, a gas oil that vaporizes completely at 880°F. (760 mm.) cannot be cracked at 880°F. at atmospheric pressure because it will be vaporized almost completely and will pass into the condenser without allowing time for cracking to occur. The products from such an operation are tar, gas oil, and a small amount of kerosene or gasoline. In order to produce mainly gasoline, the pressure must be sufficiently high to keep all materials, other than gasoline and gas, in the liquid-phase. These materials remain in the system until they are cracked into gasoline, recycle stock, or tar.

In a similar manner lubricating oils or heavy distillates can be the major products of decomposition if the pressure on the cracking system is less than atmospheric.[32] As indicated previously, the cracking reaction takes place as a series of decompositions in which the first product is lubricating oil. At high pressures the lubricating oil remains in the system and in turn is decomposed into gas oil, kerosene, and finally gasoline and gas. In other words, the decomposition continues until the decomposition products can vaporize at the temperature and pressure that are used in the cracking system. If the pressure is reduced to 30 to 100 mm., the lubricating oils that are produced during the decomposition reactions are vaporized and are automatically withdrawn from the system without decomposing into gasoline. The fact that decomposition is much more severe when gasoline is produced than when the action is stopped at intermediate stages of decomposition is illustrated by the following tabulation of yields. The tabulation shows the yields when a 10 A.P.I. Mid-Continent straight-run tar is decomposed to produce coke by using different pressures in the equipment. In each run the products were gas, coke, and the major liquid product shown below.

Run No.	Total liquid product	Per cent total distillate
. . .	Gasoline, computed from Eq. (59)	53
1	Kerosene	63
2	Gas oil (35 A.P.I.)	65
3	Lubricating oil (600 vis. at 100°)	69
4	Heavy lubricating oil (93 vis. at 210°)	72

Thus, if a large molecule is decomposed into relatively small molecules such as those in gasoline, the yield is low; whereas if the decomposition is carried only to the production of molecules such as those found in lubricating oil, the yields are considerably larger. This process differs from cracking in that a complete decomposition to gasoline is not carried out and the pressure is subatmospheric rather than above atmospheric pressure.

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[32] NELSON and FANCHER, U.S. Pat. 1,990,664.

In addition to the aforementioned purely mechanical effects of pressure, the properties of gasolines produced at a high pressure are somewhat different from those produced at a low pressure. Sachanen and Tilicheyev[33] report that the amount of unsaturated hydrocarbons found in gasoline produced at moderate cracking conditions decreases by about half as the pressure is increased from 10 to 40 atm. But at the same time the percentage of naphthene hydrocarbons increases about 12 to 16 per cent. The increase in the percentage of naphthene hydrocarbons is even greater in the cracked kerosene fraction. They also find that the yield of gasoline is slightly less at high pressures. This may be explained by the decomposition of part of the gasoline into fixed gas by the prolonged time of cracking.[34] However, Keith, Ward, and Rubin[35] and LeRoi and Ferguson[10] report just the opposite effect of pressure. Keith finds that the gas loss is three times as much at 100 as at 1,000 lb. per square inch. Commercial practice also indicates that the gas loss is less at high pressures.

Most experimenters[10,35] find that the octane number decreases as the pressure is increased if the same amount of cracking is practiced.

The use of pressure in commercial processes is necessary from a physical standpoint. Mixtures of oil and vapor at cracking conditions tend to deposit coke. Apparently the liquid segregates and collects on the walls of the tubes and is cracked for a longer time than the main body of stock. A high pressure produces a very dense vapor-phase, and hence segregation of liquid is avoided.

Liquid-phase and Vapor-phase Operation.—In general, three phase conditions are recognized in commercial processes. If the pressure is relatively low, so that a pure vapor-phase can be produced at the cracking temperature, the process may be classed as vapor-phase. Vapor-phase processes are not successful unless a vapor that is free from liquid is produced, because coke will be deposited in the tubes. At higher pressures and lower cracking temperatures a mixed-phase results and special precautions must be taken to avoid the formation of coke. Most modern commercial processes are classed as mixed-phase processes.

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[33] *Oil Gas J.*, Nov. 28, 1929, p. 46.

[34] The bomb equipment that Sachanen and Tilicheyev used promoted the cracking of gasoline by allowing part of it to condense and drip back into the cracking vessel. In some tests they kept the products of cracking in the cracking still until the test was completed.

[35] The Cracking of M. C. Virgin Gas Oil . . . Range of Temperature and Pressure, Refinery Div., *Proc. A.P.I.*, 1933.

The ideal condition, from the standpoint of heating, would be either a pure liquid- or a pure vapor-phase. If a mixed-phase is heated, it is necessary to avoid segregation of the liquid from the vapor. This may be accomplished in two ways: (1) by maintaining such a high velocity that the liquid is scoured from the heating walls or (2) by maintaining a pressure that is high enough to cause the density of the vapor to be about as large as the density of the liquid. Most of the hydrocarbons found in recycle stock and pressure distillate have critical pressures that are less than 400 lb. per square inch, and hence these materials occupy a relatively small volume even though they are in the form of vapor. In other words, the density of the vapor that is produced at a pressure of 400 lb. is nearly as great as the density of the liquid, and hence little segregation occurs.

Volume at Decomposition Conditions.—No single factor is of greater practical importance in cracking-plant design than the computation of volumes of liquids and vapors at cracking-zone conditions. Volume is directly related to time in the cracking zone and to the friction loss.

Volumes may be computed with reasonable accuracy by the use of Figs. 35 and 41–43, but careful consideration must be given to the physical properties of the stock. For example, should the gravity of the recycle stock be assumed to be 15 A.P.I. whereas the actual value is 17 A.P.I., the results may be entirely misleading. Small errors become very important, because the stocks are at or near their critical-points and a small misjudgment may shift the behavior of the material from that of a vapor to that of a liquid.

In the computation of liquid volumes the data given in Fig. 43 are not entirely adequate, because only stocks having an average characterization factor are shown. Estimates may be made, however, by constructing additional lines on Fig. 43, which pass through the known specific gravity at 60°F. and the critical-point of the material. Even better, Egloff and Nelson[36] present a reduced-temperature and -pressure chart of the density of liquids.

The extent of vaporization may be estimated by drawing flash-vaporization curves of the stocks and correcting these curves for pressure by means of the vapor-pressures of the normal paraffin hydrocarbons. Information about the distillation curves[37] of furnace feed-stocks shown in Fig. 98 is

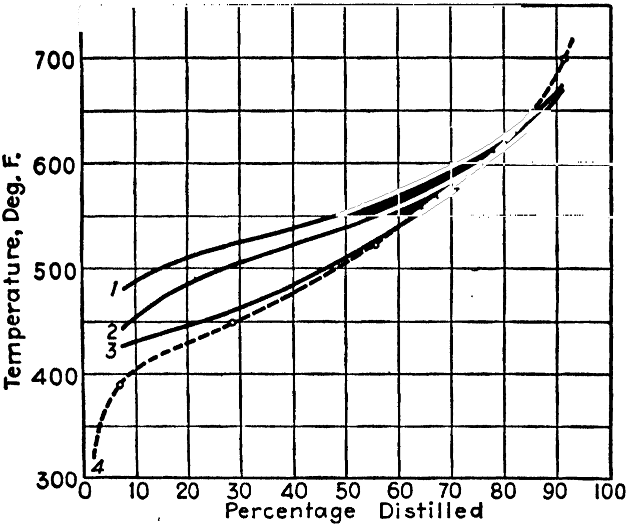

Fig. 98.—Cracking-still charge stocks.

Curve	A.P.I.	Vaporizer temperature, deg. F.	E.P. of pressure distillate, deg. F.	Recycle ratio	Kind of distillation	Source
1	20	745	440	2.4	A.S.T.M.	3 plant tests, author
2	19	745	445	1.7	A.S.T.M.	2 plant tests, author
3	24.8	...	...	3.0	A.S.T.M.	Huntington and Brown[37]
4	24.8	...	...	3.0	T.B.P.	Huntington and Brown[37]

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[36] The Modern Cracking Process, *Oil Gas J.*, July 2, 1936, p. 34.

[37] Huntington and Brown, *Ind. Eng. Chem.*, **27**, 699 (1935).

Three experimental measurements of density by Rude, Junkins, and Barnes[38] were checked by the foregoing methods of calculation with complete success.

Another factor that cannot be neglected is the volume increase (liquid volume at 60°F.) that occurs during the cracking reaction. Most cracking-stocks increase in volume by 20 to 25 per cent during cracking if the gas is considered to be liquefied (see Example 60). In the case of gaseous feed-stocks such as butane the increase in volume on a mol basis is even greater, amounting to about 100 per cent in some instances [see Eq. (61)].

In pressure-drop computations the viscosity at elevated temperatures is troublesome. The viscosities of liquids can be taken from the work of Egloff and Nelson[36] and of gases from Fig. 49, but for mixtures of liquids and vapors no truly satisfactory methods are available. In general it appears that the viscosity should be taken as nearer that of the liquid because the liquid will accumulate to some extent on the walls of the tube and because most of the friction occurs at the walls.

Example 59. Volume of Cracking-stock.—The volume of the cracking-stock studied in Examples 57 and 58 will be computed for an outlet pressure of 400 lb. per sq. in. gage and a cracking zone temperature of 915°F.

Basis: 100 gal. of reduced crude oil or 284 gal. of furnace charge. Refer to the tabulation of quantities and properties on page 324.

Estimates of the true-boiling-point distillation curves and flash-vaporization curves of the furnace inlet and outlet stocks based on the proportions given in the tabulation are shown in Fig. 99. Note that *pure recycle* was used in drawing the furnace outlet material—and that the flash curves are based on a 50 per cent boiling-point taken on a linear line between the 10 and 70 per cent points and corrected for curvature.

Inlet volume.

The pressure at the inlet to the cracking zone of the pipestill will be about 700 lb. per sq. in. gage, and the flash-vaporization curve on Fig. 99 is shown for this pressure.

It may be assumed that the entire feed material is a liquid because the small part that may be vaporized will occupy almost the same volume as it would if it were a liquid.

Density of the furnace feed at 915°F. is approximately 0.515 (Fig. 43).

$$\text{Volume of furnace feed} = \frac{2233}{0.515 \times 62.4} = 69.5 \text{ cu. ft.}$$

Outlet volume.

The 84 per cent of vaporized material consists of 8.6 per cent gas, 17.8 per cent pressure distillate, and 57.6 per cent recycle stock.

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[38] The Determination of Yield per Pass, Time . . . Density . . . in Commercial Cracking Units, *Ref. Nat. Gaso. Mfr.*, November, 1938, p. 583.

PROPERTIES OF STOCKS

	Per cent by volume		Gal.	A.P.I.	Lb.	Char-acter-ization factor	50 per cent B.P.	Mole-cular weight	Critical		Reduced		Com-pressi-bility-factor
	In	Out							Deg. F.	Lb. abs.	Temp.	Press.‡	
Fixed gas	.....	8.6	26.3*	....	79	....	...	32	....	...	....	....	1.00
Press. distillate	.....	17.8	54.0	55.0	342	11.7	230	106	565	440	1.34	0.94	0.88
Cracked tar	.....	6.5	19.9	4.8	172	10.4	810	330	1180	190	0.84	2.18	Liq.†
Gas oil	28.2	.....	80.0	27.5	593	11.9	730	345	1030	145	0.92	2.86	Liq.†
Recycle	71.8	67.1	204.0	15.0	1,640	10.5	585	226	975	300	0.96	1.38	Liq.†
Furnace charge	100.0	100.0	284.0	18.4	2,233	10.8	615	245	985	240	0.95	1.73	Liq.†

* Refer to Example 60.

† If not mixed with other materials.

‡ At a pressure of 400 lb. per sq. in. gage.

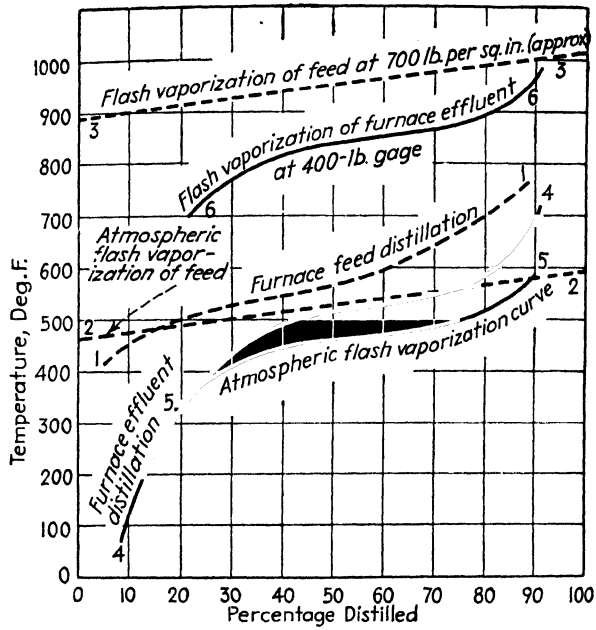


FIG. 99.—Distillation and flash-vaporization curves of furnace feed and furnace effluent stocks for Example 59.

The properties of the 57.6 per cent of recycle stock are

Characterization factor	10.5
Molal boiling point	515°F. (approx.)
A.P.I.	18.2 (Fig. 35)
Molecular weight	192
Critical temperature	912°F. (1372°R.)
Critical pressure	340 (Fig. 42)
Reduced temperature	0.997 (or 1.0)
Reduced pressure	1.22
Compressibility factor	0.22

$$\text{Mols} = \frac{0.576 \times 304.2 \times 7.87}{192} = \frac{1{,}380}{192} = 7.2$$

Density of the 18 per cent liquid portion = approximately 0.68.

$$\text{Volume of gas} \quad \frac{79 \times 1 \times 10.7 \times 1{,}375}{32 \times 415} = 87.5 \text{ cu. ft.}$$

$$\text{Volume of pressure distillate} \quad \frac{342 \times 0.88 \times 10.7 \times 1{,}375}{106 \times 415} = 100.6$$

$$\text{Volume of recycle} \quad \frac{7.2 \times 0.22 \times 10.7 \times 1{,}375}{415} = 57.2$$

$$\text{Volume of liquid} \quad \frac{(1{,}640 - 1{,}380) + 172}{0.68 \times 62.4} = \frac{432}{42.5} = \underline{10.2}$$

Volume of outlet stock = 255.5 cu. ft.

Cracking is nearly a linear function of time, and hence the average volume in the cracking zone is approximately

$$\frac{69.5 + 255.5}{2} = 162.5 \text{ cu. ft.}$$

This volume is 4.65 times larger than the liquid volume of the furnace charge-stock at 60°F. Thus, if the tube size is based on a cold oil velocity of 4 to 5 ft. per sec. (60°F.), the average velocity in the cracking zone would be about 21 ft. per sec.

Example 60. Increase in Volume during Cracking.—Example 57 provides data by which the volume increase can be computed. In this example the weight of fixed gas per 100 gal. of charging-stock was 79 lb. The density of cracked gas, if liquefied and measured at 60°F., would be approximately 3 lb. per gal.

$$\text{The volume of fixed gas (liquid)} = {}^{79}\!/\!_{3} = 26.3 \text{ gal.}$$

The total liquid yield measured at 60° is

	Gal.
Pressure distillate	54
Fuel oil (cracked)	39.9
Fixed gas	26.3
	120.2

Thus the charge increased by 20.2 per cent in volume during cracking.

Although the gas cannot be liquefied at 60°F., it may be dissolved in the other parts of the furnace stock at high pressures, and hence the volume as computed above becomes valuable for computing the volume of the cracking-stock while it is in the furnace tubes.

CHAPTER XVIII

REBUILDING HYDROCARBONS

The utilization of petroleum or of hydrocarbons as the raw stock for the manufacture of chemicals is rapidly becoming a commercial fact. Of even greater significance, petroleum products are being remade into hydrocarbon mixtures whose properties are superior to the materials originally present in crude oil. These developments have been long delayed because of the relatively unreactive nature of most petroleum hydrocarbons and because until recently only a few hydrocarbons have been isolated for study. To a large extent each type of hydrocarbon behaves differently. Hence experimenters have not been able to judge just what part of the oil was being affected, and many reactions have occurred in experiments other than the particular reactions desired. Thus, no methods have yet been devised by which all hydrocarbons, as in an oil mixture, can be rearranged into a single hydrocarbon product or even into a single type of hydrocarbon. Some commercial success has, however, been attained in utilizing the olefin hydrocarbons that are found in cracked gases. These are used for the manufacture of polymerized gasoline, alcohols, chlorinated products, and lacquer solvents, as well as small amounts of numerous other materials. An indication of the olefin content of cracked gases is given in Table 86, Chap. XXV.

Although intense interest in hydrocarbon chemistry is evident and many valuable developments have been made since 1930, as yet the study of hydrocarbon rebuilding has been centered on ascertaining what reactions can be accomplished rather than on details of operation, reaction rates, or engineering considerations. The use of numerous catalysts has also caused confusion in the correlation of engineering design data. All of these facts as well as the newness of the developments have made it impossible to present more than a bare introduction to the design of equipment for these processes. Some general data are presented in this chapter, and a few flow diagrams are presented in Chap. XXIV.

The most important reaction of all, *viz.*, decomposition or cracking, was discussed in Chap. XVII.

Types of Reactions.—Among the many types of reactions are those referred to as decomposition, dehydrogenation, polymerization, alkylation, isomerization, hydrogenation, aromatization, and cyclization. The process of *thermal decomposition*, or cracking, occupies a position of primary importance because the process has been used so extensively and because the boiling-range of crude oil is so high that it must be reduced in order to meet the market demands for gasoline.

Decomposition:

$$\underset{n\text{-butane}}{CH_3\cdot CH_2\cdot CH_2\cdot CH_3} \xrightarrow[\text{heat}]{} \underset{\text{methane}}{CH_4} + \underset{\text{propene}}{CH_3\cdot CH:CH_2}$$

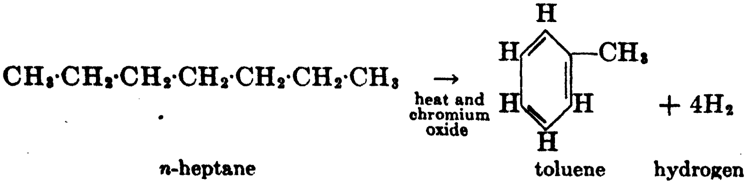
At the present time and until more is known of the reactions of the more stable types of hydrocarbons, the process of *dehydrogenation* occupies a position of primary importance. Such a reaction is the special case of decomposition in which rupture of a carbon-hydrogen bond occurs.

Dehydrogenation:

$$\underset{n\text{-pentane}}{CH_3\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_3} \xrightleftharpoons[\text{heat or catalyst}]{} \underset{\text{pentene-1}}{CH_3\cdot CH_2\cdot CH_2\cdot CH:CH_2} + \underset{\text{hydrogen}}{H_2}$$

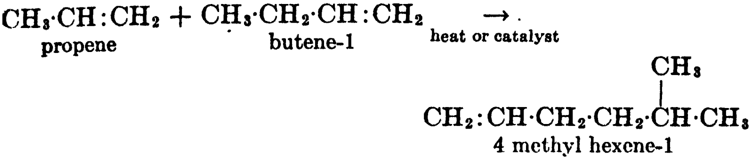
Once the stable hydrocarbons such as the paraffin and naphthenic hydrocarbons have been converted into reactive unsaturated hydrocarbons typified by the olefins, many chemical reactions or processes are possible. Dehydrogenation may occur during decomposition (see Chap. XVII, Figs. 94, 97). In a general processing scheme dehydrogenation is usually coupled with or followed by other processes such as polymerization or alkylation. Reactions that have been termed *cyclization* or *aromatization* may also be dehydrogenation reactions and may also involve decomposition, as indicated here:

Aromatization:



Polymerization has also been an important reaction because it was the first of the rebuilding reactions (except cracking) to become of commercial importance.

Polymerization:

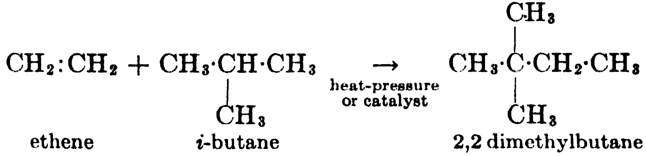


$$\underset{\text{propene}}{CH_3{\cdot}CH{:}CH_2} + \underset{\text{butene-1}}{CH_3{\cdot}CH_2{\cdot}CH{:}CH_2} \xrightarrow[\text{heat or catalyst}]{} \underset{\text{4 methyl hexene-1}}{CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}\overset{\overset{CH_3}{|}}{C}H{\cdot}CH_3}$$

Such reactions permit the manufacture of liquid gasoline from gases and in special instances the production of plastic or rubber-like materials from liquids.

Reactions by which molecules (other than olefins) are connected are termed *alkylation*—or specifically, *propylation* or *ethylation* if the alkyl radicals of propane or ethane are the reactants. The linking of a paraffin and an olefin hydrocarbon is a common example:

Alkylation:

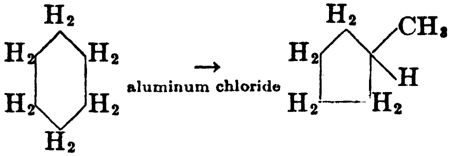


$$\underset{\text{ethene}}{CH_2{:}CH_2} + \underset{i\text{-butane}}{CH_3{\cdot}\underset{\underset{CH_3}{|}}{C}H{\cdot}CH_3} \xrightarrow[\text{or catalyst}]{\text{heat-pressure}} \underset{\text{2,2 dimethylbutane}}{CH_3{\cdot}\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}{\cdot}CH_2{\cdot}CH_3}$$

Such a process holds an advantage over polymerization because only half as many olefin molecules are required.

Isomerization reactions involve rearrangement of the molecular structure of a hydrocarbon, but nothing is added to or taken away from the material.

Isomerization:

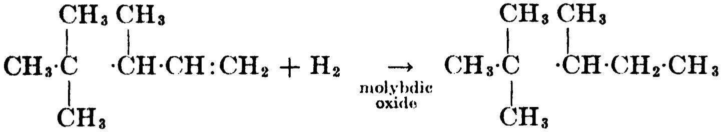


cyclohexane methylcyclopentane

Not many specific reactions of this type are available, but they probably occur along with other reactions such as cracking, polymerization, and alkylation but cannot be recognized because of the other reactions and because of the difficulty in identifying the hydrocarbon products.

The process of *hydrogenation* may be utilized in adding hydrogen to unsaturated hydrocarbons. It has not found wide application because most oils are already saturated with hydrogen to a sufficient degree. Nevertheless, it will find increasing application as the reactions listed above are applied more widely.

Hydrogenation:



$$\mathrm{CH_3\cdot}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\cdot\overset{\mathrm{CH_3}}{\mathrm{CH}}\mathrm{\cdot CH{:}CH_2} + \mathrm{H_2} \xrightarrow[\text{oxide}]{\text{molybdic}} \mathrm{CH_3\cdot}\overset{\mathrm{CH_3}}{\underset{\mathrm{CH_3}}{\mathrm{C}}}\cdot\overset{\mathrm{CH_3}}{\mathrm{CH}}\mathrm{\cdot CH_2\cdot CH_3}$$

2,2,3 trimethyl pentene-4 hydrogen 2,2,3 trimethylpentane

It has already been used in connection with thermal decomposition (cracking) as a means of adding hydrogen to the residue of tar that is produced in cracking so that greater yields are possible. When used in this way it is referred to as *destructive hydrogenation*.

Catalytic cracking probably involves several or most of the foregoing reactions—certainly decomposition, polymerization, alkylation, and isomerization. All of these reactions take place at about the same temperature, and the effect of a suitable catalyst is to lower the temperature of all the reactions. Any wholesale treatment of mixtures of hydrocarbons must employ operating conditions and catalysts that are a compromise between the conditions that are best for each of the many reactions taking place.

When no catalyst is employed, the temperatures at which decomposition, dehydrogenation, alkylation, polymerization, and isomerization take place are nearly the same, or in the range of 800 to 1100°F. Even with catalysts, several of the reactions such as hydrogenation and dehydrogenation, and some isomerization reactions must be conducted in this same range of temperature in order to obtain commercial yields.

In addition to the hydrocarbon-rearrangement reactions listed above, a large number of operations such as desulfurization, nitration, sulfonation, chlorination, and oxidation are being developed.

REACTION VELOCITY

Little information about the rates of reaction for the various processes can be given because experimental data are lacking, and hence it is valuable to know the general kinetic relationships of various types of reactions. These reactions are not complicated for constant-volume reactions (nearly true for liquids), but they become cumbersome and nearly useless as a means of correlating data if the volume is not constant, as is the case for many gaseous reactions. Fortunately, most reactions are not conducted to completion, and hence at yields-per-pass of 25 or 50 per cent the failure of the volume to remain constant does not introduce serious errors. In all the derivations that follow the reaction is assumed to be taking place at a constant temperature. Perhaps the greatest usefulness of the following derivations is to point out the general mathematical forms to use in developing empirical formulae of the rate of reaction.

Rates at Constant Volume.—For a unimolecular reaction of which pure decomposition is an example, the rate of reaction is directly dependent on the amount of reactant material that is left at any time during the reaction.

$$A \rightarrow B + D + \cdots$$

The rate at which the concentration of A decreases with time is a constant function of the concentration designated as c_A:

$$\frac{-dc_A}{dt} = k_1 C_A$$

and if the initial concentration of A is designated as a, the amount of A that has reacted during a time t is designated as x, and $(a - x)$ is the concentration of A after a time of t:

$$\frac{-dc_A}{dt} = \frac{-d(a - x)}{dt} = k_1(a - x)$$

and by integration

$$k_1 = \frac{1}{t} \ln \frac{a}{a - x} \qquad (67)$$

When possible it is best to use the concentration in mols, but liquid volume or weight per cent can be used with fair accuracy (see Fig. 94) for first-order, or unimolecular, reactions.

Similarly for bimolecular (second-order) reactions at constant volume, pressure, and temperature

$$A + B \rightarrow D + E + \cdots$$
$$\frac{dx}{dt} = k_2(a - x)(b - x)$$

and

$$k_2 = \frac{1}{t(a - x)} \ln \frac{b(a - x)}{a(b - x)} \tag{68}$$

in which a and b are the initial concentrations of A and B in mols per unit volume and x is the number of mols of A and B that react with one another during a time t. In the special case in which A and B are present in stoichiometric proportions or if two molecules of the same material react with one another (polymerization), the second-order equation simplifies to

$$2A \rightarrow D + E + \cdots$$
$$\frac{dx}{dt} = k_2(a - x)^2$$

and

$$k_2 = \frac{1}{t} \frac{x}{a(a - x)} \tag{69}$$

Note that pressure enters into the reaction velocity constant for gaseous reactions as an inverse function because the units of a, b, and x are mols per unit volume (or density).

The order of a reaction may be determined by inserting experimental data in the equations and noting which equation gives the most constant value of k. A discussion of other methods of determining reaction order and a discussion of the kinetics of higher order reactions are given in the "Chemical Engineers' Handbook."[1]

Rates at Varying Conditions.—In most gaseous reactions the volume does not remain constant and modified equations are required. Note, however, that if the conversion-per-pass is low or the system is diluted with some unreactive material such as a recycle stock, the volume change may be so small that the reaction behaves essentially as a constant volume one.

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[1] **Perry, J. H., Editor in Chief, McGraw-Hill Book Company, Inc., New York, 1934.**

In the case of a unimolecular reaction at a varying volume[1] the constant is

$$k_1 = \frac{vV}{V_b} \ln \frac{1}{1 - x} - (v - 1)x \qquad (70)$$

where V = volume of gas entering per second at contact conditions.

V_b = entire volume of reaction space.

v = mols of product produced from 1 mol of reactant material.

x = fraction of reactant material that undergoes reaction.

The relationships for higher order reactions are extremely complicated, and hence it has become common usage to employ the so-called "space velocity" as a measure of reaction rate or capacity. The space velocity is defined as the ratio of the volume of inlet material to the volume of the reaction space. Thus, if no change in volume or temperature occurs during the reaction, the time of reaction is

$$\text{Time, sec.} = \frac{\text{volume of feed per sec.}}{\text{space velocity}}$$

If the volume or temperature (absolute) are assumed to vary according to a linear function, the time can be approximated by using the average of the inlet and outlet volumes rather than the volume of feed.

In systems in which the temperature varies, the rate can be described approximately by equations such as Eq. (69) (page 332), but the situation can usually be handled more accurately by means of a series of computations each of which embraces a short range of temperature. Each short range of temperature can be handled at a weighted average temperature.

Effect of Temperature on Rate.—The effect of temperature is to double the rate for a rise in temperature of about 10°C. The influence of temperature is, however, a function of the particular reaction, and at elevated temperatures a larger number of degrees is required to double the rate. The change in reaction velocity with temperature can usually be described by the Arrhenius equation:

$$\frac{d \ln k}{dT} = \frac{A}{RT^2}$$

or for ranges in temperature through which A is constant:

$$\ln k = \frac{-A}{RT} + B \tag{71}$$

or

$$k = Be^{\frac{-A}{RT}}$$

where A = a characteristic constant (−53,500 cal. per g.-mol for gas oil) referred to as the "energy of activation."

T = absolute temperature, deg C.

R = the gas law constant (1.987).

B = a constant (about 28.8 for gas oil).

A convenient way of correlating data is to plot the logarithm of the reaction velocity constant versus the reciprocal of absolute temperature. This yields a substantially straight line (Fig. 94, page 306) having a slope of $-A/2.303R$.

THERMODYNAMICS OF REACTIONS

Most of the hydrocarbon-conversion processes are still in the development stage, and this is particularly true of the higher molecular weight materials, which constitute the bulk of petroleum. For these reasons, it is of primary importance to be able to judge the feasibility of proposed reactions or processes and to compute (or estimate) other thermal factors such as the heat of reaction. These factors can be evaluated by means of thermodynamics, and in time it may be possible to develop processes by which whole series of hydrocarbons can be converted into other series of hydrocarbons in a selective manner or by a number of consecutive processes to convert one series of hydrocarbons after another, until the entire mixture is converted into a single type of material.

Feasibility of a Reaction.—The possibility that a reaction may occur can be judged by means of the free energy of the materials that are involved in the reaction. The free energy change may be considered as a measure of the tendency of a reaction to occur. The standard free energy change designated as ΔF° may be defined as the free energy change of the reaction if each of the materials involved in the reaction is assumed to be at unit activity. Mathematically the free energy, mass-law equilibrium constant and thermodynamic constants are related by

$$\Delta F^\circ = -RT \ln K = \Delta H - T\Delta S \tag{72}$$

where ΔF° = standard free energy change of reaction.
ΔH = heat of reaction (exothermic is negative).
ΔS = entropy change of reaction.
T = absolute temperature.
K = equilibrium constant.
R = gas constant = 1.987 cal. per mol-deg.

If the value of ΔF° is found to be negative, the value of K will be relatively large and the yield will also be large when and if equilibrium is established. As ΔF° approaches zero or becomes positive, the value of K and of the yield at equilibrium becomes smaller and smaller. If ΔF° is negative, the reaction is a promising one; if ΔF° is zero, the usefulness of the reaction is doubtful but may justify further study; but if the value of ΔF° is greater than 10,000, in most instances such a process would not be feasible. It will also be noted that temperature exerts an important influence on the value of ΔF°, and hence the foregoing situations may be altered by the use of another temperature.

No idea of the rate at which the reaction will occur is possible from a consideration of free energies, and hence many of the reactions that are found to be thermodynamically feasible do not occur at a practical rate or they may require the use of catalysts or an activating influence in order to cause the reaction to attain equilibrium within a reasonable length of time. Nevertheless, the examination of a process or reaction by these thermodynamic methods will indicate the feasibility of the reaction and thus save time and energy in studying reactions experimentally that hold little promise of success.

The mass-law equilibrium constant of a reaction is designated as

$$aA + bB + \cdots = cC + dD + \cdots$$

$$K = \frac{a_C^c a_D^d \cdots}{a_A^a a_B^b \cdots} \tag{73}$$

in which a is the activity. At moderate pressures, however, the activity of a gas is approximately equal to its partial-pressure in atmospheres or to mol percentage, so that

$$K = \frac{p_C^c p_D^d \cdots}{p_A^a p_B^b \cdots}$$

TABLE 48.—FREE ENERGIES OF FORMATION OF HYDROCARBONS[*]
Cal. per g.-mol

Substance	Formula	ΔH_f° (heat of formation, 298°K.)	ΔF° at 298°K.	ΔF° at 500°K.	ΔF° at 1000°K.
Methane	CH_4	−17,865	−12,300(−12,085)	−8,050(−8,050)	3,450(3,450)
Acetylene	C_2H_2	58,228	50,840(50,034)	48,100(47,160)	41,300(40,850)
Ethylene	C_2H_4	12,556	15,820(16,279)	18,520(18,830)	27,670(26,700)
Ethane	C_2H_6	−20,191	− 8,260(−7,787)	1,960(−50)	25,790(24,190)
Propene	C_3H_6	4,956	14,820(14,730)	22,510(20,930)	43,380(40,340)
Propane	C_3H_8	−24,750	− 6,220(−5,550)	7,540(5,640)	45,200(41,300)
Butadiene 1-3	C_4H_6	26,865	(33,960)	(40,000)	(60,000)
Isobutene	C_4H_8	− 3,205	14,240(14,440)	26,970(25,500)	62,780(58,720)
Butene-1	C_4H_8	383	16,780(16,810)	29,440(27,000)	62,960(58,230)
Butene-2 (cis)	C_4H_8	− 1,388	14,860(15,570)	27,440(26,290)	60,800(58,590)
Butene-2 (trans)	C_4H_8	− 2,338	14,450(14,800)	27,390(25,640)	61,650(58,240)
Isobutane	C_4H_{10}	−31,350	− 4,900(−4,160)	14,670(11,440)	67,350(60,680)
n-Butane	C_4H_{10}	−29,715	− 5,000(−3,630)	13,500(11,070)	63,170(58,300)
Pentadiene 1-4	C_5H_8	25,565	40,220	57,000	
Pentene-1	C_5H_{10}	− 4,644	17,800	36,000	80,000
Isopentane	C_5H_{12}	−36,671	− 4,230(−3,190)	19,850	85,300
n-Pentane	C_5H_{12}	−34,739	− 2,570(−1,620)	21,040	85,670
Tetramethyl-methane	C_5H_{12}	−39,410	− 4,500(−3,310)	21,180(17,760)	90,950(84;020)
Benzene	C_6H_6	....	30,640	38,700	59,600
Cyclohexene	C_6H_{10}	....	19,400	32,100	
Hexene-1	C_6H_{12}	....	19,200	42,000	99,100
Cyclohexane	C_6H_{12}	....	8,030	34,600	103,500
Methylcyclopentane	C_6H_{12}	....	3,700	21,500	
2-Methylpentane	C_6H_{14}	−41,800	(−1,000)		
n-Hexane	C_6H_{14}	−40,010	− 1,500(80)	28,000	103,000
2,2-Dimethylbutane	C_6H_{14}	−44,400	(−2,300)		
Toluene	C_7H_8	....	28,400	41,200	74,200
Heptene-1	C_7H_{14}	....	20,720	48,720	118,400
Ethylcyclopentane	C_7H_{14}	....	8,000		
Methylcyclohexane	C_7H_{14}	....	4,280(l)		
2-Methylhexane	C_7H_{16}	−47,100	− 1,300(600)	35,700	
3-Methylhexane	C_7H_{16}	....	− 930	36,350	
3-Ethylpentane	C_7H_{16}	....	− 130	37,050	
2,2-Dimethylpentane	C_7H_{16}	−49,800	− 130(−300)	38,300	
2,3-Dimethylpentane	C_7H_{16}	....	− 430	37,100	
2,4-Dimethyl-pentane	C_7H_{16}	....	370	38,500	
3,3-Dimethylpentane	C_7H_{16}	....	− 730	37,300	
2,2,3-Trimethylbutane	C_7H_{16}	....	870	40,000	
n-Heptane	C_7H_{16}	−45,350	190(1,750)	35,000	122,500
Ethylbenzene	C_8H_{10}	....	28,090(l)		
m-Xylene	C_8H_{10}	....	29,660	47,300	92,800
Diisobutene (low B.P.)	C_8H_{16}	....	21,530	56,090	146,700
Diisobutene (high B.P.)	C_8H_{16}	....	22,260	58,450	150,200
2,2,4-Trimethylpentane	C_8H_{18}	−56,200	1,570(700)	46,000	
n-Octane	C_8H_{18}	−50,700	1,520(3,400)	40,000	141,600
n-Nonane	C_9H_{20}	....	2,280(l)		
n-Decane	$C_{10}H_{22}$	....	3,490(l)		
2-Methylnonane	$C_{10}H_{22}$	....	2,000(l)		
Decylene-2	$C_{10}H_{20}$	....	24,100(l)		
n-Butylcyclohexane	$C_{10}H_{20}$	....	7,000(l)		
n-Butylbenzene	$C_{10}H_{14}$	....	29,670(l)		
Naphthalene	$C_{10}H_8$	....	47,430(S)50,400	62,000	93,500
Undecane	$C_{11}H_{24}$	....	4,310(l)		
Dodecane	$C_{12}H_{26}$	....	6,530(l)		
n-Heptylcyclohexane	$C_{13}H_{26}$	....	9,530(l)		
Anthracene	$C_{14}H_{10}$	....	64,190(S)72,400	89,200	135,000
Hexadecane	$C_{16}H_{34}$	....	10,710(l)		
Dotriacontane	$C_{32}H_{66}$	....	31,300(l)		

---

[*] The free energies are for gases except when followed by (l) and (S), which designate liquids and solids. Parentheses around the numbers indicate that they were determined by statistical mechanics and were taken from Reference 6.

Approximate values of the activities or corrected partial pressures of gases at elevated temperatures and pressures are given by Hougen and Watson.[2]

Values of Free Energy.—From Eq. (72) it appears that ΔF° can be determined in three general ways, *i.e.*, from entropies and heats of reaction, from equilibrium data, or from correlations of the free energy values of materials that have already been examined experimentally. Only the last method is of much value for the purpose of investigating the feasibility of a reaction, although in some instances it may be possible to compute approximate free energies by computing ΔS and ΔH.

Not many values of free energy are available at the present time, but several generalizations[3,4] have been developed.

For n paraffin hydrocarbons:[3]

$$\Delta F_T^\circ = 10{,}550 - 5{,}890n + 25.2nT - 2.2T$$

For olefin-1 hydrocarbons:[3]

$$\Delta F_T^\circ = 20{,}321 - 5{,}835n + 24.52nT - 33.26T$$

For simple naphthene hydrocarbons:[4]

$$\Delta F_T = 10{,}375 - 8{,}633n + 26.09nT - 15.9T$$

For acetylene hydrocarbons:[4]

$$\Delta F_T^\circ = 70.425 - 8{,}633n + 26.09nT - 67.5T$$

A somewhat more useful type of approach[5] involves the use of the free energy change required to produce various bondages (even branch-chain) such as those given in Eqs. (74*a*)–(74*d*). In all of these equations n refers to the number of carbon atoms and T to the temperature in °K.

C—H bonds.[5]

$$\Delta F_T^\circ = -3{,}344.5 + 2.97T \ln T - 0.0023T^2 + 0.000000188T^3 - 13.68T \quad (74a)$$

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[2] "Industrial Chemical Calculations," John Wiley & Sons, Inc., New York, 1936.

[3] THOMAS, EGLOFF, and MORRELL, Thermodynamics in Hydrocarbon Research, *Ind. Eng. Chem.*, **29**, 1260 (1937).

[4] FRANCIS and KLEINSCHMIDT, Application of Thermodynamics to Chemical Reactions of Petroleum Products, *Proc. A.P.I.*, December Meeting, 1929.

[5] BRUINS and CZARNECKI, Relation between Structure and Free Energy of Organic Molecules, *Ind. Eng. Chem.*, **33**, 201 (1941).

C—C bonds.[5]

$$\Delta F_T = 4.437 + 0.421T \ln T + 0.0017T^2 - 0.00000062T^3 + 9.53T \quad (74b)$$

C═C bonds.[5]

$$\Delta F_T^\circ = 28{,}024 + 2.75T \ln T - 0.0014T^2 - 0.00000080T^3 - 24.86T \quad (74c)$$

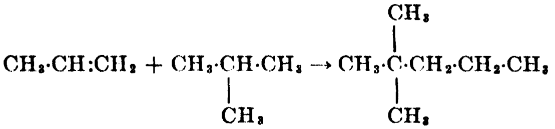
C—CH₃ bonds.[5]

$$\Delta F_T^\circ = -7{,}624 + 10.42T \ln T - 0.0057T^2 - 0.000000015T^3 - 36.12T \quad (74d)$$

Values for particular hydrocarbons are given in Table 48,[3,6,7] which includes many estimated values but which appears to be the best data that are now available. More data on the effect of branch chains and ring attachments are badly needed.

In using free energies for examining the feasibility of a reaction, the free energies of the reactants are subtracted algebraically from the free energies of the products of the reaction as in Example 61.

Example 61. Feasibility of a Reaction.—The possibility of making 2,2-dimethylpentane from propene and isobutane will be investigated.



$$CH_3{\cdot}CH{:}CH_2 + CH_3{\cdot}\underset{\displaystyle CH_3}{\underset{|}{CH}}{\cdot}CH_3 \rightarrow CH_3{\cdot}\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}{\cdot}CH_2{\cdot}CH_2{\cdot}CH_3$$

From Table 48:

	ΔF°_{298}	ΔF°_{500}
$C_3H_6(g)$	14,820	22,510
$iC_4H_{10}(g)$	− 4,900	14,670
C_7H_{16}	− 130	38,300

For the entire reaction:

$$\Delta F^\circ_{298} = -130 - 14{,}820 - (-4{,}900) = -10{,}050$$
$$\Delta F^\circ_{500} = 38{,}300 - 22{,}510 - 14{,}670 = 1{,}120$$

Thus, the preceding reaction appears to be possible at temperatures of 25 to 227°C. but may require the use of a catalyst. The reaction should proceed more completely at low temperatures (free energy is negative), but the rate may be so slow that higher temperatures may be necessary. The

[6] Pitzer, K. S., Chemical Equilibria, Free Energies and Heat Contents for Gaseous Hydrocarbons, Symposium on Fundamental Chemical Thermodynamics, A.C.S., Cincinnati Meeting, April, 1940.

[7] Parks, G. S., Some Free Energy Data for Typical Hydrocarbons . . . , Symposium on Fundamental Chemical Thermodynamics, A.C.S., Cincinnati Meeting, April, 1940.

application of pressure should assist the reaction because it is a bimolecular one.

The numerical values of K are useful in deciding upon a suitable temperature:

$$\ln K_{298} = \frac{-10{,}050}{-RT} = \frac{-10{,}050}{-1.987 \times 298} = 17$$

K_{298} is very large, or the yield approaches 100 per cent.

$$\ln K_{500} = \frac{1{,}120}{-1.987 \times 500} = -1.128$$

$$K_{500} = \frac{(C_7H_{16})}{(C_3H_6)(iC_4H_{10})} = 0.3236$$

Solving for percentage of C_7H_{16} after establishing equilibrium,

$$A + B \rightleftarrows C$$

Let x = mols of C (or C_7H_{16}) in reaction products per mol A introduced
Mols $A = 1 - x =$ mols B

At equilibrium:

$$0.3236 = \frac{x}{(1 - x)^2}$$

$$x = 0.2045 \text{ mols}$$

Percentage of C_7H_{16} in products:

Total mols after reaction $= (1 - x) + (1 - x) + x = 2 - x$

$$\text{Percentage} = \frac{0.2045 \times 100}{2 - 0.2045} = 11.4 \text{ per cent } C_7H_{16}$$

This is not an economical yield in most instances.

Values at other temperatures may be estimated by assuming that ΔF° is a linear function of temperature; *i.e.*, $\Delta F^\circ = aT + b$. The constants a and b in such an equation may be evaluated thus:

at 298°

$$-10{,}050 = 298a + b$$

at 500°

$$1{,}120 = 500a + b$$

subtracting

$$-11{,}170 = -202a$$

$$a = 55.3 \text{ and } b = -26{,}530$$

and

$$\Delta F^\circ = 55.3T - 26{,}530$$

If in this instance a yield of 30 per cent is feasible by practicing recycling, the temperature at which the process can operate can be estimated as follows:

Mols of C_7H_{16} produced when 1 mol of A is processed:

$$30 \text{ per cent} = \frac{100x}{2 - x}$$

$$x = 0.4615 \text{ mols of } C_7H_{16}$$

$$\text{Equilibrium constant} = K = \frac{0.4615}{(1 - 0.4615)^2} = 1.596$$

Also

$$\ln K = 0.46749 \qquad \frac{\Delta F^\circ}{-RT} = \frac{55.3T - 26{,}530}{-1.987T}$$

and

$$T = 471^\circ \text{ abs. or } 198^\circ\text{C.}$$

Thus it would appear that the alkylation of propene by isobutane is thermodynamically possible in the temperature range of about 200°C. and lower. The ultimate yield at 200°C. is not large; but since the rate or velocity of the reaction increases rapidly with temperature, it will probably be best to operate at as high a temperature as possible. Should the rate be too slow at 200°C., a catalyst must be found.

From a purely thermodynamic standpoint it might also be possible to make 2,3-dimethylpentane, 2,4-dimethylpentane, 3,3-dimethylpentane, or even 2,2,3-trimethylbutane from propene and isobutane. The values of the free energies for these reactions (computed in the same manner) are

	ΔF°_{298}	ΔF°_{500}
2,3-Dimethylpentane	−10,350	−80
3,3-Dimethylpentane	−10,650	120
2,2-Dimethylpentane	−10,050	1,120
2,4-Dimethylpentane	− 9,550	1,320
2,2,3-Trimethylbutane	− 9,050	2,820

Thus it appears that several reactions might take place simultaneously but that the amounts of each of the isomers (at 500°K.) would be somewhat in the decreasing order shown in the foregoing tabulation. Even this does not include all of the thermodynamic possibilities, because there are many other isomeric seven-carbon-atom hydrocarbons.

When data on ΔF° are not available, they can be computed by means of the ΔH and $T\Delta S$ terms in Eq. (72). The heat of reaction, or ΔH, may be computed from heats of combustion (or formation) as discussed later, but the entropy change designated by ΔS presents more difficulty. In a practical way the absolute entropy designated as S consists of the sum of all heat energy inputs involved in heating from absolute zero temperature, each energy quantity being divided by the absolute temperature at which the energy is added. All inputs of energy such as those involved in changes of crystalline state at low temperatures, energy or heat of fusion, and heat of vaporization must be included, as well as the sensible heats of the solid, liquid, and vapor. It is usually necessary to approximate the sensible heat at low temperatures (near absolute zero) by extrapolation and to hope that no changes in the crystalline state of the material are involved in this temperature range. Such computations are discussed in chemical thermodynamics texts and particularly by Parks and Huffman.[8]

Heat of Reaction.—The heat of reaction may be computed by determining the algebraic sum of the heats of combustion (or formation) of the materials before and after the reaction as in Example 55 (page 298). If the products contain more chemical energy than the reactants, the reaction is endothermic and vice versa. Data for heats of combustion (or formation) may be obtained from handbooks, from "Physical Constants of the Principal Hydrocarbons,"[9] or from the numerous papers by Rossini and others that are listed at the end of this chapter. Typical heats of reaction are given for particular reactions in the remaining parts of this chapter.

TYPICAL HYDROCARBON PROCESSES

Unfortunately most of the hydrocarbon-conversion processes are still undergoing development, and hence not much engineering design data are available. In many instances the relative importance of the various proposed processes is not clear, nor have all workers been equally free in disclosing information. At this stage it is even impossible to generalize as to the types of catalysts that should be used for various processes. Somewhat more specific information about plant arrangements is given in Chap. XXIV.

Polymerization.—This reaction occurs in several ways, *i.e.*, as bimolecular or polymolecular reactions or as successive reactions that produce dimer, trimer, and polymer products:

$$2C_2H_4 \rightarrow C_4H_8$$
$$3C_2H_4 \rightarrow C_6H_{12}$$
$$C_4H_8 + C_6H_{12} \rightarrow C_{10}H_{20}$$

Russell and Hottel[10] conclude that the polymerization of ethylene in the early stages is bimolecular but that some third-order combinations also take place. Egloff[11] has examined polymer gasoline to determine the size of molecule that is produced:

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[8] "Free Energies of Some Organic Compounds," Reinhold Publishing Corporation, New York, 1932; also R. H. Ewell, *Ind. Eng. Chem.*, **32**, 778 (1940).

[9] Technical and Research Division of the Texas Company, 1939.

[10] Rate of Ethylene Polymerization, *Ind. Eng. Chem.*, **30**, 183 (1938).

No. of Carbon Atoms	Per Cent
3–4	0
5	1.7
6	5.6
7	48.1
8	15.2
9	0
10	0
11	0
11 plus	12.3 (some lighter hydrocarbons)
Loss	17.1 (sudden leak)

Rate of reaction data[10,12,13,14,15] was correlated as shown in Fig. 100 for ethene, propene, and the butenes. It is more convenient to use percentage rather than concentration as the unit of a and x in Eq. (69), and hence a pressure term was introduced into the correlation as shown in Eq. (75). The pressures employed by these experimenters ranged from atmospheric to over 3,000 lb. per square inch absolute. No catalysts were intentionally used by these experimenters, but some catalytic action may have been produced by the vessel walls. The reaction velocity constant divided by pressure, shown in Fig. 100, is related to time and yield as follows:

$$\frac{K_2}{P} = \frac{1}{tP}\frac{x}{a(1-x)} \tag{75}$$

where K_2/P = reaction velocity constant divided by pressure (read from Fig. 100).
t = time, min.
P = pressure, lb. per sq. in. abs.
x = fraction of olefins reacting in time t.
a = fraction of olefins contained in feed-stock.

No such simple relationship is apparent when catalysts are used. Apparently the condition of the catalyst, the intimacy of contact between the gas and catalyst, and secondary effects of temperature such as the formation of resins or coke on the catalyst all confuse the mechanism of catalytic polymerization. Rate of reaction, however, is not extremely important because the percentage conversion is usually high if enough catalyst is

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[11] EGLOFF, G., Polymerization a Major Factor in Tomorrow's Super Fuels, *Nat. Petroleum News*, Oct. 14, 1936, p. 30.

[12] SULLIVAN, RUTHRUFF, and KUENTZEL, *Ind. Eng. Chem.*, **27**, 1072 (1935).

[13] DUNSTAN, HAGUE, and WHEELER, *Ind. Eng. Chem.*, **26**, 307 (1934).

[14] WHEELER and WOOD, *J. Chem. Soc.*, p. 1819 (1930).

[15] FROLICH and WIEZEVICH, *Ind. Eng. Chem.*, **27**, 1055 (1935).

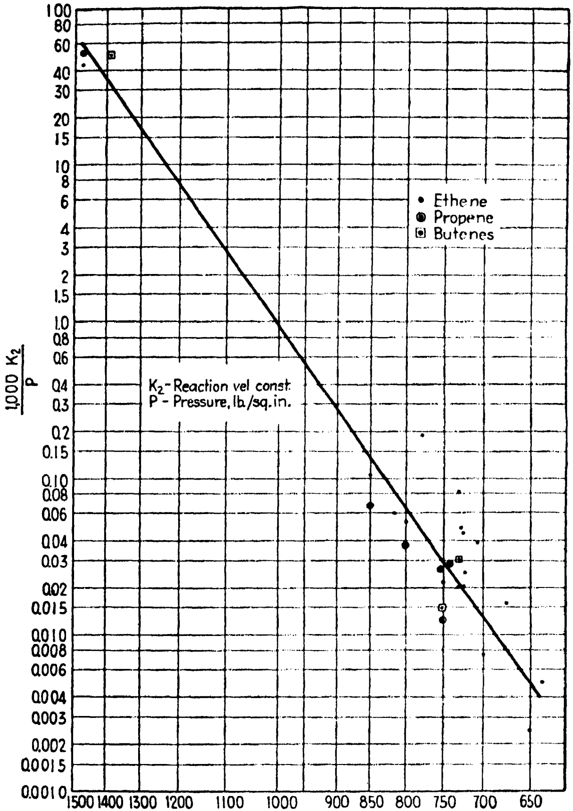

FIG. 100.—Reaction velocity constants for polymerization.

used to permit long operating runs and because the reaction temperature may be adjusted upward as the catalyst becomes spent. In the case of the solid phosphoric acid catalyst of the Universal Oil Products Company, the effect[16] of catalyst temperature on olefin conversion is

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[16] SHANLEY, and EGLOFF, Midget Polymerization and Midget Isooctane Units, *Ref. Nat. Gaso. Mfr.*, June, 1939, p. 227.

Average Catalyst Temperature, Deg. F.	Olefin Conversion, Per Cent
406	76.5
415	82.0
421	80.5
423	84.4
428	88.3
429	90.0
445	92.8
452	95.0

Orthophosphoric acid is one of the most active polymerization catalysts. It tends to lose water and form inactive metaphosphoric acid at temperatures above about 450°F. Vaporization of water may be suppressed somewhat by the use of 2 to 10 per cent steam in the olefin feed-stock, but larger amounts will cause the formation of alcohols. Solid forms of phosphoric acid catalysts[17] may consist of admixtures of kieselguhr, starch, magnesia, alumina, zinc chloride, zinc oxide, etc., calcined at 180 to 250°C. The solid catalyst may be regenerated by passing a carefully controlled stream of diluted air through the material at temperatures approaching 650°F. followed by steaming. Hot spots will cause acid loss by volatilization. In recent plants as much as 70 gal. of polymer gasoline have been produced per pound of catalyst before regeneration is necessary.

Sulfuric acid is also used for polymerization.[18] Acid of 65 to 70 per cent strength is contacted with the liquid hydrocarbons at about 170°F. The acid is recycled in proportions of 1.5 parts of acid to 1 of oil. The acid is not destroyed in months of operation, and only a small amount of make-up acid to care for mechanical losses is necessary.

The heat of reaction (exothermic) for polymerization is about 40,000 B.t.u. per pound-mol for each union of two molecules. This figure appears to be a constant regardless of the types of molecules that combine.

Dehydrogenation.—The equilibrium established between a paraffin hydrocarbon and the hydrogen and olefin produced from it by dehydrogenation have been studied extensively.[19] The percentage of dehydrogenation that takes place at various temperatures is given in Table 49.

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[17] NASH and HOWES, "Principles of Motor Fuel Preparation and Application," 2d ed., Vol. I, p. 438, John Wiley & Sons, Inc., New York, 1938.

[18] MCALLISTER, S. H., The Catalytic Polymerization of Butylenes by Sulfuric Acid, *Ref. Nat. Gaso. Mfr.*, November, 1937, p. 493.

TABLE 49.—PERCENTAGE COMPLETION OF DEHYDROGENATION REACTION AT EQUILIBRIUM

Temperature, deg. C.	Ethane	Propane	*n*-Butane	*i*-Butane
427	1.6	6.4	11.0	12.2
500	5.4	18.6	29.2	31.9
600	19.5	53.6	69.8	72.1
727	57.5	89.8	95.2	95.2

Note that a dehydrogenation of 95 per cent as shown for 727°C. does not mean an olefin yield of 95 per cent. According to the dehydrogenation reaction the analysis of the product gas would be 5 per cent unreacted paraffin hydrocarbon and 47.5 per cent each of the olefin and the hydrogen gases.

Catalytic methods of dehydrogenation are receiving attention because of the extremely high temperatures and pressures required for the thermal process (see Fig. 94). Catalysts that have been employed are the oxides of aluminum, chromium, copper, barium, and molybdenum, and orthophosphoric acid. Alumina prepared by calcining specially crystallized alumina trihydrate is used at 600 to 650°C. for propane or isobutane. Chromium oxide in the form of its active gel is highly selective in its action but is destroyed by temperatures exceeding 500°C. If alumina is used as the carrier for 10 to 20 per cent chromium oxide, the dehydrogenation reaction proceeds at even 50 to 70°C. but the life of the catalyst is short. Both the activated alumina and the alumina-chrome catalysts may be regenerated by careful oxidation of the impurities in a stream of air (diluted with nitrogen) for as many as 200 regenerations.[20] The life of the catalyst is greatly improved by introducing small amounts of water vapor. For the dehydrogenation of isobutane using alumina,

[19] FREY and HUPPKE, *Ind. Eng. Chem.*, **25**, 54 (1933); KASSEL, L. S., *J. Chem. Phys.*, **4**, 276, 438 (1936); and PITZER, K. S., *J. Chem. Phys.*, **5**, 473 (1937).

[20] WILLIAMS, E. C., Dehydrogenation in Petroleum Industry, Am. Chem. Soc., Baltimore Meeting, April, 1939.

0.1 mol per cent of water vapor is the optimum. Iron, cobalt, nickel, and some other metals promote the formation of carbon and hydrogen at temperatures of 300 to 700°C., but these metals are being used in commercial cracking equipment, etc., without causing destructive decomposition. Perhaps the failure of these metals to cause difficulty results from the formation of a protective film of sulfide or carbon.

Grosse, Morrell, and Mavity[21] report the successful dehydrogenation of olefin hydrocarbons into diolefin hydrocarbons. Such hydrocarbons may become useful in producing synthetic rubberlike materials.

When using chromium oxide supported on alumina, Grosse and Ipatieff[22] find that a conversion of 90 to 95 per cent paraffin hydrocarbons into olefins can be accomplished at 500 to 600 deg. C. Nearly pure hydrogen gas is the waste gas. The rate is very much faster than by thermal dehydrogenation. The rate of reaction[23] is somewhat as shown in Table 50 when operating at 1 atm. pressure.

TABLE 50.—RATE OF DEHYDROGENATION *i*-Butane[23]

Temperature, deg. C.	Percentage dehydrogenation for these space velocities (volume of *i*-butane per hr. per volume of catalyst space)						
	100	400	1,000	4,000	10,000	40,000	100,000
500	26	11.5	5	1			
550	..	42.0	28.5	10	4.5		
600	..	....	65.0	40	21.0	6.0	2.5
650	..	....	....	79	60.0	25.0	12.0
675	..	....	....	..	80.0	43.0	23.0

The dehydrogenation of the paraffin hydrocarbons may be carried far enough to produce aromatic hydrocarbons[24] by the use of chromium trioxide, molybdenum oxides, and vanadium oxides supported on activated alumina at 550°C. Yields of 90 per cent toluene from heptane are claimed by recycling operations. Such processes may provide an abundant supply of aromatics (or cycloparaffins) for the manufacture of explosives, dyes, medicines, and innumerable aromatic products.

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[21] Catalytic Dehydrogenation of Monoolefins to Diolefins, *Ind. Eng. Chem.*, **32**, 309 (1940).

[22] Catalytic Dehydrogenation of Gaseous Paraffins, *Ind. Eng. Chem.*, **32**, 268 (1940).

[23] GROSSE, IPATIEFF, EGLOFF, and MORRELL, Catalytic Dehydrogenation Process, *Oil Gas J.*, Nov. 23, 1939, p. 53.

[24] GROSSE, MORRELL and MATTOX, Catalytic Cyclization of Aliphatic Hydrocarbons to Aromatics, *Ind. Eng. Chem.*, **32**, 528 (1940).

Destructive Hydrogenation.—The hydrogenation of animal and vegetable oils at relatively low pressures by the use of activated nickel, platinum, or palladium catalysts involves the direct union of hydrogen. In the case of mineral oils or coal, it is also usually advisable to decompose or crack the oil to some extent as well as to hydrogenate, in order to make lower boiling products (gasoline) or to rebuild the structure of the molecule. Thus, cracking temperatures (800 to 950°F.) and high pressures (3,000 lb. up) are employed, and special catalysts that are not poisoned by sulfur are necessary.

A common method of producing hydrogen is by the reaction of steam and methane to give hydrogen and carbon monoxide. Newman and Jacob[25] find the equilibrium to be as follows:

$$\log K = \log \frac{P_{CO} \times P_{H_2}^3}{P_{CH_4} \times P_{H_2O}} = \frac{-10,300}{T} + 4.87 \log T$$
$$+ 0.000066T - 0.00000081T^2 - 3.04$$

In order to obtain good yields at temperatures below 1000°C., catalysts are necessary. Nickel or cobalt catalysts promoted by alumina[26] and supported on some refractory such as fire clay or magnesia brick are good catalysts, but they are somewhat sensitive to hydrogen sulfide.

The destructive hydrogenation of crude petroleum stocks as referred to above permits the production of products that have almost any desirable properties such as high octane number, high Viscosity Index, or high solvency-power naphthas, but the process is so expensive that it cannot be widely used at the present time. The real usefulness of hydrogenation at our present stage of development is as an adjunct to other processes such as polymerization. As an example, one method of producing high-octane fuels is by catalytic dehydrogenation of gaseous paraffin hydrocarbons into olefins, polymerization of the olefins into hydrocarbons of the gasoline range, followed by catalytic hydrogenation to produce a stable final product. For such operations the activated nickel catalyst[27] mentioned above can be used because sulfur can be removed from the incoming gases. Such a catalyst[27] may be prepared by impregnating porcelain with hydrated nickel nitrate. The nitrate is then converted into the oxide by heating and reduced in a stream of hydrogen to elemental nickel. It must be kept in an atmosphere of hydrogen when not in service. If stocks that contain sulfur must be handled, recourse must be had to such catalysts as molybdic trioxide, molybdic acid, or chromium oxides supported on charcoal or pumice.[28] Catalysts of this nature are said to be used in the destructive hydrogenation of crude petroleum stocks.

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[25] *Z. Elektrochem.*, **30**, 557 (1924).

[26] FISCHER and TROPSCH, *Brennstoff-Chem.*, **9**, 39 (1928); MAREK and HAHN, "Catalytic Oxidation of Organic Compounds in the Vapor Phase," p. 27, Chemical Catalog Company, Inc., New York, 1932; and HAWK, GOLDEN, STORCH, and FIELDNER, *Ind. Eng. Chem.*, **24**, 23 (1932).

The hydrogenation reactions are highly exothermic. The heats of reaction for hexene to hexane and benzene to cyclohexane are 644 B.t.u. and 1360 B.t.u. per pound of feed-stock, and similar values can be computed from heats of combustion or formation.

Alkylation.—The direct union of olefin and paraffin hydrocarbons by the process referred to as alkylation is favored by high pressures and low temperatures. However, in order to accomplish the reaction without catalysts a temperature of about 900 to 975°F. is required.[29] Polymerization occurs actively at this temperature, and hence the concentration of olefins must be kept low. Thermal alkylation is conducted at 3,500 to 8,000 lb. per square inch, whereas by means of catalysts such as boron fluoride,[30] aluminum chloride,[31] or the double halides of alkali metals with aluminum[32] pressures less than 1,000 lb. per square inch and temperatures ranging from 450°F. down to below zero may be employed. Sulfuric acid is widely used as a catalyst in commercial installations.[33] The process operates at 30 to 50°F. for butenes and at substantially atmospheric pressure. The acid consumption is higher for reactions involving propene, and hence this reaction awaits further study. The olefin content of the feed is usually kept at 20 to 40 per cent, and the ratio of acid to hydrocarbon is about 1 to 1. The strength of the make-up acid is 98 per cent, but it becomes diluted during use. A contact time of 5 min. appears to be sufficient, but commercial equipment is built for 20 to 40 min.

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[27] ANON., Catalytic Hydrogenation of Octenes to Octanes, *Oil Gas J.*, May 26, 1938, p. 50.

[28] NASH and HOWES, Principles of Motor Fuel Preparation and Application, 2d ed., Vol. I, p. 337, John Wiley & Sons, Inc., New York, 1938.

[29] OBERFELL and FREY, Thermal Alkylation and Neohexane, *Oil Gas J.*, Nov. 23, 1939, p. 50.

[30] EGLOFF and MORRELL, Alkylation of Hydrocarbons, Symposium on Role of Catalysts . . . , Am. Chem. Soc., Baltimore Meeting, April, 1939.

[31] IPATIEFF, GROSSE, PINES, and KOMAREWSKY, *J. Am. Chem. Soc.*, **58**, 913 (1936).

The acid alkylation process works most successfully on the higher molecular weight olefins (such as the butenes), whereas thermal alkylation attacks ethene most readily. Acid alkylation is limited to the isoparaffin hydrocarbons (isobutane and isopentane), but the thermal process handles either the iso or the normal compounds.

Isomerization.—An enormous number of isomerization reactions have been reported,[34] but most of them have not been studied quantitatively. An example is the reaction of butene-1 and -2 into isobutene in the presence of a phosphoric acid catalyst. The equilibrium constants[35] for this reaction are given by the following equation:

$$\log K_p = \log \frac{(\text{isobutene})}{(\text{butene-1}) + (\text{butene-2})} = \frac{304}{T} - 0.528$$

Another example is the work of Glasebrook and Lovell[36] on the equilibrium between cyclohexane and methylcyclopentane in the presence of aluminum chloride. The ratios of methylcyclopentane to cyclohexane at equilibrium are as follows:

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[32] Blunck and Carmody, Catalytic Alkylation of Isobutane with Gaseous Olefins, *Ind. Eng. Chem.*, **32**, 328 (1940).

[33] Birch, Dunstan, Fidler, Pim, and Tait, Condensation of Olefins with Isoparaffins in Sulfuric Acid, *Oil Gas J.*, June 23, 1938, p. 49; also *Oil Gas J.*, Nov. 17, 1939, p. 104.

[34] Egloff, Komarewsky, and Hulla, Hydrocarbons and Their Isomerization, Symposium on the Role of Catalysts . . . , Am. Chem. Soc., Baltimore Meeting, April, 1939.

[35] Serebriakova and Frost, *J. Gen. Chem.* (U.S.S.R.), **7**, 122 (1937).

[36] The Isomerization of Cyclohexane and Methylcyclopentane, *J. Am. Chem. Soc.*, **61**, 1717 (1939).

Deg. C.	K
25	0.143
35	0.170
45	0.193
55	0.238
65	0.272
77.4	0.344

The conversion of hydrocarbons from straight-chain structures to branched-chain or ring structures is of great commercial importance because the latter structures have higher octane numbers than the straight-chain compounds.

Catalytic Cracking and Reforming.—At the present time these processes are being applied primarily to gas oil stocks of low carbon-residue content and to gasoline or naphtha stocks for reforming into higher octane-number material. A once-through operation produces from 35 to 90 per cent gasoline depending upon the boiling-range of the feed-stock, and the gas oil produced in such operations is processed in regular thermal cracking equipment along with residual stocks.

An enormous number of materials act as catalysts for catalytic cracking, and some of these have been known for many years.[37] The difficulty has been that the life of the catalyst is only a few minutes because of carbon deposition, and even today the catalytic processes must be operated on a cycle of operation such as (1) 10 min. of service, (2) 10 min. of steaming, and (3) 10 min. of revivification of the catalyst. Among the available catalysts are naturally occurring clays, bauxite, alumina, and silicate materials, and oxides of chromium, tungsten, and vanadium. The rate of reaction is primarily dependent upon the life of the catalyst, and hence the regular formulations of reaction rate are of little value.

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[37] Friedel and Crafts, *Ann. chim. phys.*, **6** (I) 440, 446, 449, 461, 510, 518 (1844); McAfee, A. M., *Ind. Eng. Chem.*, **7**, 737 (1915); Ipatieff, V. N., *J. Russ. Phys.-Chem. Soc.*, **38**, 63 (1900); and for general reference, Leslie, E. H., "Motor Fuels," Chemical Catalog Company, Inc., New York, 1923.

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CHAPTER XIX

DISTILLATION PROCESSES

All petroleum distillation processes are fundamentally the same. The process engineer can make no headway in initiating new processes or in truly understanding the flow diagrams of processes until this fact is clearly understood. In the main, all distillation processes require the following essential units of equipment: (1) pipestills or other heaters, (2) fractionating towers, (3) steam stripping columns, (4) heat exchangers, (5) condensers and coolers, (6) pumps and connecting lines, and (7) storage and accumulator tanks. However, in adapting these units of equipment to the processing of a particular stock, many factors must be considered. Among the most important of these are

1. The boiling-range of the stock.
2. The stability of the stock with respect to heat.
3. The specifications of the products to be produced.

Boiling-range of Stock.—Some stocks boil at such a high temperature that they cannot be vaporized at atmospheric pressure without decomposing them, and other stocks must be kept under pressure or they will vaporize at room temperature. Raw natural gasoline contains relatively large amounts of gaseous hydrocarbons and is an example of a stock that must be distilled under pressure. These hydrocarbons must be removed if a stable low-vapor-pressure natural gasoline, which will perform suitably as a motor fuel, is to be produced. The gaseous hydrocarbons are most effectively removed by fractionation; but the gaseous hydrocarbons are the overhead product from the column, and they cannot be kept in the liquid state unless pressure is applied. Hence natural-gasoline stabilizers are operated at 125 to 300 lb. per square inch pressure, and the reflux material consists of the volatile hydrocarbons ethane, propane, butane, etc. Of course, the top of the column could be kept at a low temperature by refrigeration, but such methods have not proved practical. The temperature in the reflux condensers is governed by the temperature of the cooling water. The pressure that is used is dependent on the vapor-pressure of the reflux material at the temperature that exists in the condenser.

With high-boiling stocks the opposite difficulty arises. Vigorous decomposition starts to take place at temperatures exceeding about 710°F., and for this reason many stocks such as reduced or topped crude oil, tars, and heavy crude oils cannot be distilled at

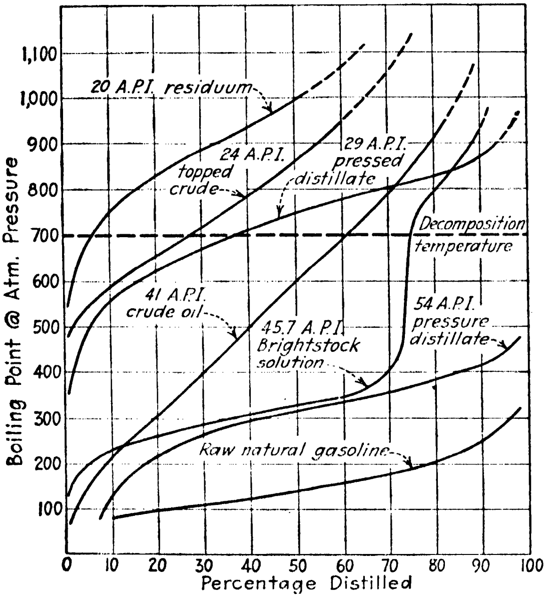

FIG. 101.—Distillation ranges of typical Mid-Continent stocks.

atmospheric pressure. These stocks have such high boiling-ranges that they must be distilled in a vacuum or by the use of large amounts of steam. Some cannot be distilled unless both steam and vacuum are employed.

Between these two extremes are stocks such as crude oil, pressure distillate, pressed distillate, brightstock solution, and special naphtha stocks, which can be distilled at atmospheric pressure but which may require the use of some steam. Figure 101 indicates the relative boiling-ranges of typical Mid-Continent stocks. In distilling crude oil for gasoline, kerosene, and a part of the gas oil, a pipestill-outlet temperature of about 740°F. may be required. Thus a small amount of steam is normally required to keep the temperature down to 710°F. This results in a vaporizer temperature in the tower of about 660°F. For other stocks, commonly used vaporizer and outlet temperatures are given in Table 51.

TABLE 51.—VAPORIZER TEMPERATURES

Stock	Products	Temperature		Pressure, lb. per sq. in. or mm.	Steam
		Vaporizer	Heater outlet		
1. Natural gasoline........	Gas	210	230	120–200	No
2. Pressure distillate.......	Gasoline	275	325	Atmospheric	Yes
3. Crude oil..............	Light oils	660	710	Atmospheric	Some
4. Pressed distillate........	Neutral oils	670	710	Atmospheric	Yes
5. Brightstock solution.....	Naphtha and neutral	670	710	Atmospheric	Yes
6. Reduced crude..........	Lub. oils	690	730	30–80 mm.	Yes
7. Fuel oil or tar..........	Asphalt residue	730	770	30–80 mm.	Yes
8. Fuel oil or tar..........	Distilled cracking-stock	775	850	Atmospheric	Yes

Thus modifications of the simple fractionating system are necessary for all except a few stocks. Some stocks require a pressure so that a low-boiling reflux material can be condensed, and others require a vacuum and steam.

Sensitive Stocks.—Although the boiling-range of a stock is an important factor, the sensitiveness of the stock to high temperatures must also be considered. All stocks start to decompose at about 680°F., yielding lower boiling products, but even lower temperatures may cause discoloration. In distilling crude oil a slight discoloration of the products is not important because most of the products receive chemical treatment before they are sold. Likewise, discoloration is not important in the distillation of a reduced crude oil for the production of a gas oil cracking-stock or for the production of asphalt. However, in distilling treated pressure distillate, pressed distillate, or brightstock solution, a discoloration during distillation cannot be allowed because the products are usually sold without further treatment. If treatment follows these distillations, then the cost of the treatment will be increased by the discoloration.

High temperatures also result in a loss of heavy lubricating oil stock. The yield of lubricating oils is often decreased by 10 to

15 per cent by the use of too high temperatures. A mild decomposition takes place in which light lubricating oil and gas oil are produced from the heavy stocks.

Treated pressure distillate is particularly sensitive to high temperatures. Redistillation should not be conducted at temperatures exceeding 375°F., and many refiners find that a maximum temperature of 275°F. is economical because of the reduction in treating costs.

In the manufacture of asphalt most refiners limit the temperature to 770°F. Nevertheless, the temperature that may be used without ruining the ductility of the product is greatly dependent upon the characteristics of the stock and upon the manner of heating. One refiner has successfully used a temperature of 835°F. at the pipestill outlet, but others have found that 770°F. was too high.

The engineer must bear in mind that some stocks are very different from others. The most satisfactory operating temperature can be determined only by experiments with the particular stock. A factor that cannot be neglected when considering temperature is the time that the oil is held at the high temperature. As mentioned above, some asphalt stocks may be heated to 835°F. without damage if the time at the elevated temperature is short. If the stock is held at this temperature for more than a few minutes, extensive cracking will occur and the operation will become a cracking process. Thus the temperature that can be attained without serious decomposition is dependent to some extent upon the time. Although a lubricating oil stock can be heated to 710 or even 740°F. in a low-absorption-rate pipestill heater, this same temperature, if maintained in a shellstill, will cause serious losses in yield and a discoloration, the removal of which may necessitate a costly chemical treatment.

Flow Diagrams and Operating Conditions.—The remaining pages of the chapter are devoted to the common processing systems. The systems that are presented are not necessarily the best for all conditions. In fact, in some cases they are presented merely because they are novel or because they illustrate principles that would otherwise be neglected. The best performance cannot be obtained from a unit unless it is "tailor-made" for the particular stock and for the particular market and plant environment in which it must function.

The operating conditions are likewise of a general nature, although in most cases they are actual conditions that have been recorded in plant operation. The operating conditions will be different for each stock that is encountered. The evaluation curves that are shown with each process are discussed in Chap. VII.

A survey of the processing methods used in refineries appears to show that there are as many methods as there are refineries. Nevertheless, upon close inspection these many methods are found to be essentially the same, and the major differences are in the arrangement and shape of the equipments rather than in the manner of operation. In most refineries the processing methods are the result of years of development; and although the processing methods may be modern, the equipment that is used may appear to be obsolete. This is often the result of the use of existing shellstills, towers, chambers, coolers, etc., from antiquated equipment. They appear obsolete; but if they are properly utilized, they may perform as satisfactorily as modern, new equipment.

Topping or Reducing Crude Oil.—In many ways the initial break-up of crude oil into raw products is the most simple distillation process. Certainly it is the most widely known operation. In the past, shellstills, with or without fractionating towers, were commonly used. Today the shellstill is never installed, but old shellstills are often utilized in conjunction with pipestills.

A modern topping unit is shown in Fig. 102, and the evaluation curves of a typical Pennsylvanian crude oil are shown in Fig. 103. The oil is pumped continuously through the heat-exchange system at a pump pressure of 125 to 200 lb. per square inch, through the tubestill, and into the vaporizer section of the multiple-draw fractionating tower. At this point the temperature must be sufficiently high to cause vaporization of all of the products that are collected at points above the vaporizer, and the temperature may be a little higher, so that about 20 per cent of the bottoms stock is also vaporized. The purpose of the additional vaporization is to provide better fractionation on the plates that are situated just above the vaporizer. Without excess vaporization, very little reflux will exist at these plates and no reflux will flow from the plate above the vaporizer into the vaporizer section. Reflux is circulated through the top of the column. The hot reflux material is drawn from the tower,

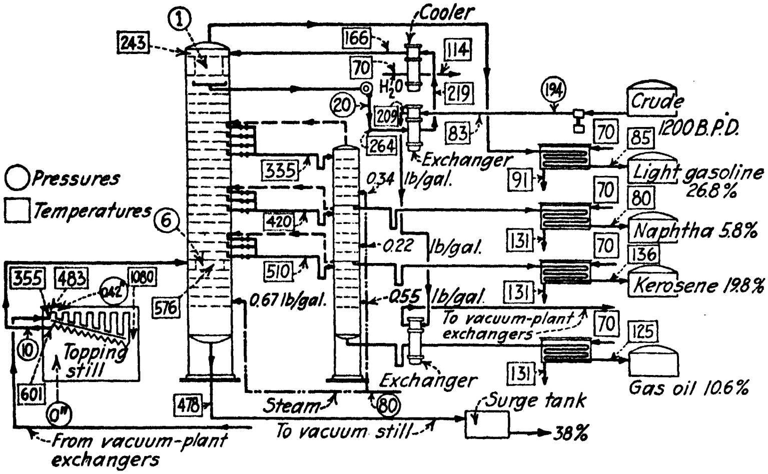

FIG. 102.—Continuous pipestill topping plant. (*A. J. Smith Engineering Company.*)

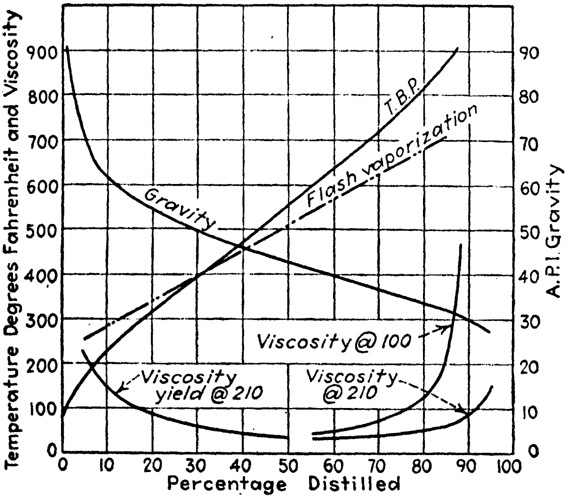

FIG. 103.—Typical paraffin-base crude oil. (Not the crude oil processed in Fig. 102.)

cooled by a heat exchanger and a water cooler, and returned to the tower. It serves to cool and condense the vapors that arise from the vaporizer. The recirculating type of reflux shown in Fig. 102 is not the most common method of removing reflux heat, but it is an excellent method for certain conditions. Various means of removing reflux heat are described on page 464. The plates above the vaporizer or feed-plate act as rectifying plates, but the plates below the feed are steam stripping plates. Steam is admitted below or on the bottom tray, and the low-boiling materials in the vaporizer residue are removed so that a high flash-point bottom product is produced. The steam ascends the tower, and at the vaporizer it is effective in lowering the vaporizer temperature.

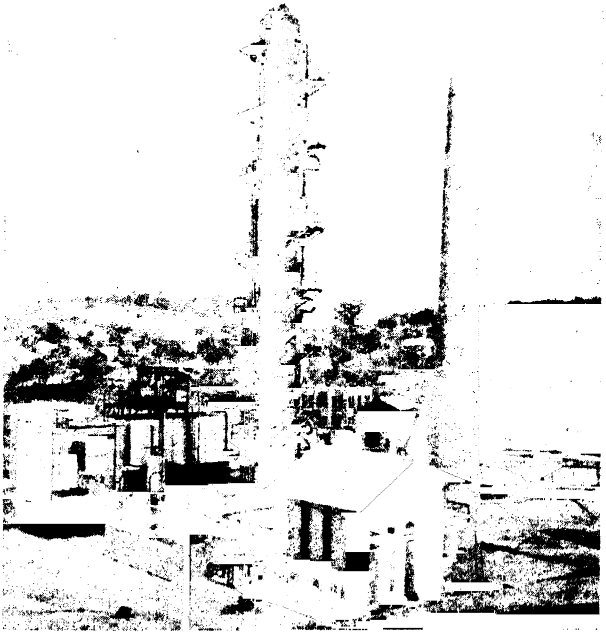

FIG. 104.—Modern topping plant. (*Arthur G. McKee and Company.*)

The system as shown in Fig. 102 is not limited to the production of five overhead products. As many as eight products have been withdrawn from a single tower. Furthermore, by the use of a large amount of steam, such heavy stocks as wax distillate and even cylinder stock may be vaporized from crude oil. However, the vaporizer temperature must be high (800 to 870°F.),[1] and such temperatures result in discoloration and losses by decomposition. The difficulties with dewaxing are also troublesome. Plants operating at atmospheric pressure for the manufacture of distilled cylinder stocks have never been entirely successful, but many refiners distill wax distillate at atmospheric pressure.

Heat-exchange.—The number of heat exchangers that may be wisely utilized depends upon the quantities and temperatures of the several products. In general, a heat exchanger should pay for itself within a period of two years. In complete plants, which conduct vacuum and cracking operations as well as the topping of crude oil, the crude oil may be advantageously heated by products from these other units because they are at a relatively high temperature. In conjunction with a vacuum plant, the crude oil may be pumped through the condenser exchangers in the topping plant, through the reflux and partial condensers of the vacuum plant, and finally back to the topping-plant pipestill. In this manner and in more elaborate heat-exchanger systems, such as those which involve bottoms exchangers or exchangers in cracking plants, the temperature of the crude oil may be raised even to 500°F. Thus for certain low-boiling crude oils the topping pipestill may be eliminated entirely. In the same manner the enormous quantity of heat available in a cracking unit and at a high temperature level as well may be used to advantage. Although such an extensive use of heat-exchange appears to be advantageous, such systems are not without disadvantages. The dependency of several units upon one another is a serious complication. Thus if one unit must be shut down, the other unit or units must be shut down or operated in a crippled condition. Sometimes these plants are constructed with extra heating equipment so that any one of the plants can be operated independently, but the extra heaters cost almost as much as if they had been originally provided instead of exchangers. Exchangers may also be a source of great expense unless they are wisely chosen and the stocks are clean and noncorrosive.

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[1] One plant operated at 870°F., distilling a 160 viscosity at 210 cylinder stock, but the color was so poor and the loss of heavy stock was so great that the operation was discontinued.

In the extreme, exchangers could be utilized on every tray of a fractionating tower as well as on each of the products and perhaps succeed in attaining a thermal efficiency of 60 to 80 per cent. One such system[2] succeeded in operating without condensers. The real merit, however, of such a system depends upon the cost of installing and maintaining the heat-exchange system, and it is doubtful if such a system is economically feasible in view of the low cost of heat in most refineries. Extra trays would also be required in a fractionating tower employing such a large amount of heat-exchange because the tower would operate with very little reflux.

Pressure-still Distillate.—The raw distillate from cracking plants is a foul-smelling, dark-colored material that must be treated and redistilled or immediately mixed with a gum inhibitor before it can be sold as a motor fuel. After acid treatment, the distillate is still a bright-yellow-colored material. Although part of the coloring material is high boiling and may be separated by distillation, some of it decomposes if a high temperature is used and causes discoloration of the distillate. Gumlike materials are also produced at high temperatures. These difficulties are apparently caused by the decomposition and hydrolysis of alkyl sulfates which are produced during acid treatment. The exact temperature below which discoloration and the formation of gum occur depends upon the chemical nature of the distillate, the manner in which the chemical treatment was conducted, and the way in which heat is applied. In the face of these many factors it is not surprising to find that little data are available regarding the exact temperature to be used in redistillation. This problem has been met by each refiner by conducting laboratory studies of the cracked distillate. Trusty[3] shows the effect of steam on the color of the finished distillates, but unfortunately the maximum temperatures are not included in the paper. With this particular distillate, the effect of increasing the steam,[4] other conditions and operations being the same, was as follows:

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[2] ZIEGENHAIN, W. T., No Condensers Used in Topping Unit, *Oil Gas J.*, Dec. 18, 1930, p. 30.

[3] Acid Treatment of Cracked Distillates . . , *Ref. Nat. Gaso. Mfr.*, August, 1932, p. 455.

[4] The sulfur content of the distillate was lower when more steam was used.

Per Cent Steam in Overhead	Color
0	18
5	22
20	25

Refiners usually limit the temperature for redistillation to 325°F., although some plants have been operated at 375°F. The tendency has been to decrease the temperature because the treating operation is much simplified if the temperature is low.

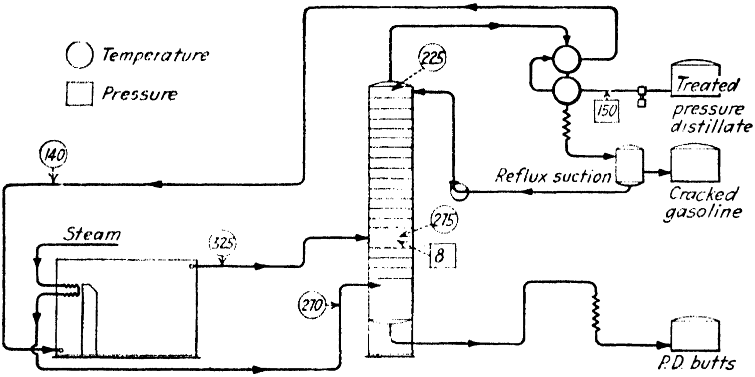

Fig. 105.—Pipestill pressure distillate rerun unit.

Several companies have installed vacuum systems[5] in which the temperature is limited to 275°F. The vacuum redistillation systems are usually of the two-stage type, in which part of the distillate is distilled at atmospheric pressure and the heavier part is vaporized in a second fractionator which operates at a reduced pressure. Laboratory tests indicate that discoloration may occur at even 150°F.

Many small refiners continue to redistill pressure distillate in shellstills, but all newly erected plants are of the continuous pipestill and fractionator type of design, as shown in Fig. 105 (see also Fig. 106). The method of removing reflux heat, as shown in Fig. 105, is the most satisfactory and generally used method.

Debutanizers.—Pressure-still distillate is usually condensed and collected under pressure, and part of the gas from the cracking unit is absorbed by the pressure distillate. The pressure in the gas separator (15 lb. or higher) causes the gas to dissolve to such an extent that the pressure distillate usually has a vapor-pressure of 10 to 25 lb. per square inch. Burket[6] presents the analyses of pressure distillates that were collected at different pressures as shown in Table 52.

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[5] Noll, H. D., *Oil Gas J.*, Mar. 31, 1932, p. 66.

TABLE 52.—ANALYSES OF PRESSURE DISTILLATES*

	Volume percentage analyses of pressure distillates collected at pressures of, lb. per sq. in.			
	14.7	30	40	165
A.P.I.	52.6	58.2	55.3	61.3
Methane	.....	0.02	0.06	0.47
Ethane	0.33	0.24	0.69	2.22
Propane	3.4	1.63	3.22	5.67
Butanes	8.43	9.39	9.33	10.31
Pentanes	10.93	13.11	12.05	11.26
Hexanes and heavier	76.91	75.61	74.65	70.07

* The distillates were not from the same charging-stock.

All of these distillates contain appreciable quantities of propane and butane and will exert vapor-pressures that make them undesirable for blending purposes. In order to reduce the vapor-pressure, many refiners are installing debutanizers or pressure-distillate stabilizers.

If low-vapor-pressure natural gasoline is used for blending or if an excess of naphtha blending stock is available, then the pressure distillate may not need to be stabilized. The pressure at which the distillate is collected from the cracking plant, as indicated above, is of great importance. Nevertheless, it is hardly practical to collect the distillate at pressures of less than 20 lb. per square inch, because the gas cannot be easily handled at lower pressures. The fractionation of pressure distillate is conducted in a manner similar in all respects to the stabilization of raw natural gasoline (Fig. 108). However, pressure distillate contains less propane and butane than raw natural gasoline, and hence the feed must be heated to a higher temperature. The raw pressure distillate is usually stabilized before acid treatment, and the lowest boiling part of the distillate is sometimes collected from the stabilizer and incorporated into gasoline, without undergoing acid treatment.

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[6] P.D. Stabilization . . . , *Ref. Nat. Gaso. Mfr.*, March, 1931, p. 75.

Reboilers.—In fractionating two component feed-stocks a part or sometimes all of the heat input is supplied at the bottom of the fractionator. The theories discussed in Chap. XV were

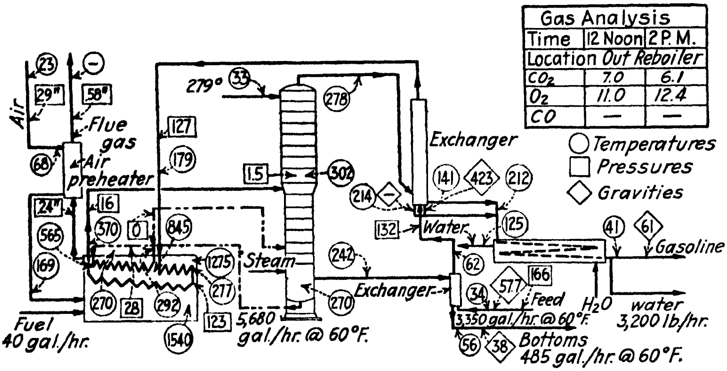

FIG. 106.—Pressure distillate rerun unit with reboiler arrangement (see Fig. 107). (*E. B. Badger and Sons Company.*)

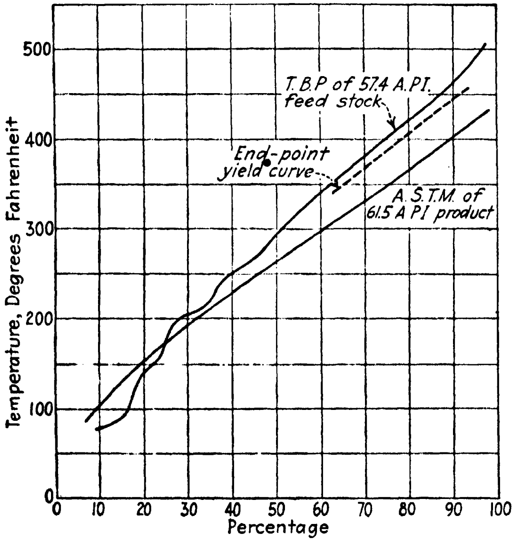

FIG. 107.—Evaluation curves of pressure distillate (see Fig. 106).

based upon such a process system. In such systems the part of the column below the feed, *viz.*, the exhausting section, effects some separation. The lower part of most petroleum oil columns does not function as a fractionator but as a simple steam stripping section. At frequent intervals flow diagrams are proposed in which heat is supplied at the bottom of petroleum oil towers. Oil is circulated from the bottom of the tower, through a few tubes in the pipestill or other heating equipment, and back into one of the lower plates of the tower. Reboilers do increase the efficiency of fractionation, but a satisfactory degree of separation can usually be obtained more cheaply by the use of a stripping section. The use of two coils in a pipestill is a difficult problem. The exact heat input in each coil can hardly be determined except by experiments with the pipestill during operation. This has often caused reboiler installations to perform poorly, with the result that reboiling has never been widely used.

Figure 106 indicates a reboiler arrangement as used in redistilling pressure distillate, and Fig. 107 shows the analyses of the feed and distillate. Reboilers heated by steam are used in stabilizer towers for natural gasoline, pressure distillate, butane-propane mixtures, and some solvents. In these cases the bottoms product must be well fractionated, whereas in most of the processes that have been discussed heretofore the fractionation of the overhead product was most important. Fractionators for the production of special cuts, such as solvents, are frequently operated with reboilers or with fired shells at the bottom of the towers.

Natural-gasoline Stabilizer.—The natural-gasoline stabilizer or fractionator is one of the best examples that the industry offers of the application of the fundamentals of distillation, as discussed for two-component systems in Chap. XV. Nevertheless, the feed to a stabilizer always consists of at least six components so that the application of the equations for two-component systems is difficult. Heat is supplied at the bottom of the tower by a steam reboiler; and if the feed is heated by heat-exchange with the stabilized gasoline, no additional preheating of the stock may be necessary. An effective separation of butane from the lighter hydrocarbons is necessary, and hence a large number of trays are used in the tower. Even though many trays are used, a high reflux ratio is necessary. In a few refineries a side-stream product or a part of the reflux is collected and subsequently separated into commercial butane, bottle gas (largely propane), etc. A typical stabilizer diagram is shown in Fig. 108.[7] The diagram shows more plates than are normally used.

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[7] Burdick, G., *Oil Gas J.*, Apr. 9, 1931, p. 26.

The recent developments of polymerization, dehydrogenation, alkylation, etc., processes, which are now practiced primarily on gaseous hydrocarbons, all require high-pressure fractionators similar to stabilizers. Thus, stabilizers are used in natural-gasoline plants, in refinery gas-recovery systems, for pressure-distillate debutanization, and in many hydrocarbon-conversion processes. In several of the conversion processes it is necessary to produce pure hydrocarbons, and hence such elaborate systems as that shown in Fig. 109 are sometimes necessary.[8] The

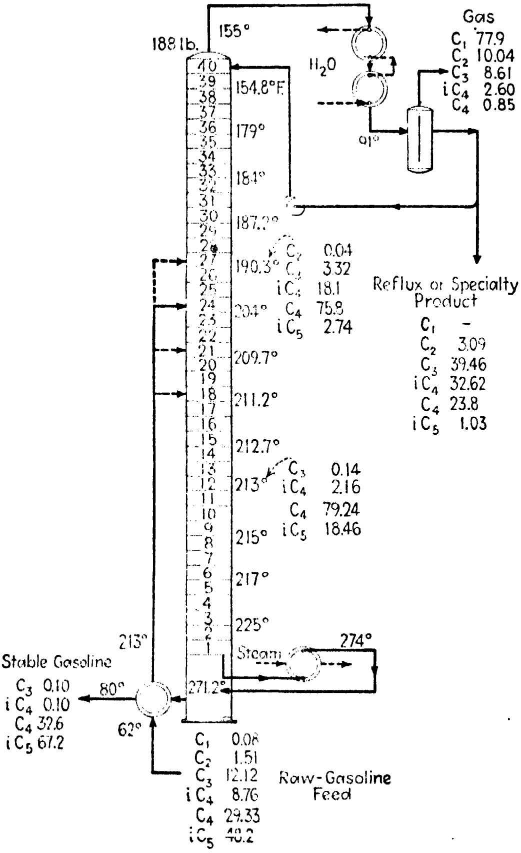

FIG. 108.—Natural-gasoline stabilizer. (*Burdick, Oil Gas J.*)

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[8] TURNER and RUBEY, Light Hydrocarbons . . . , *Ref. Nat. Gaso. Mfr.*, September, 1938, p. 423.

process was used primarily for making an isobutane-butane feed for polymerization units, but uses for propane and isopentane were also contemplated. Data concerning the four columns are:

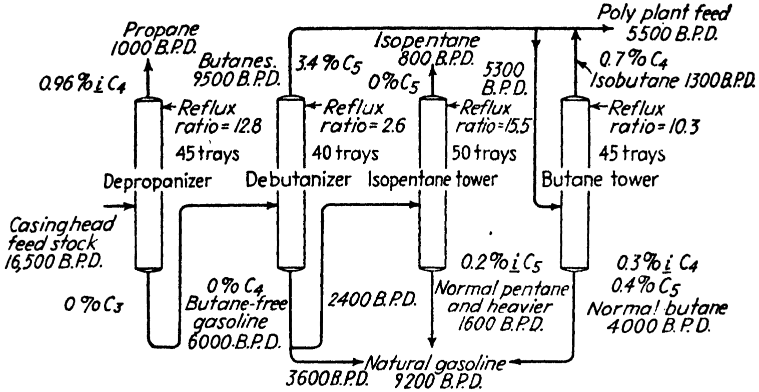

FIG. 109.—Typical fractionation system for separating a number of pure hydrocarbons. (*After Turner and Rubey.*)

	Column I depropanizer	Column II debutanizer	Column III isopentane	Column IV butanes
Capacity, bbl. per day	10,450	10,160	2,266	2,900
Impurities, in overhead, per cent	$0.96C_4$	$3.5C_5$	$0.0nC_5$	$0.7nC_4$
	......	$0.0C_3$	$0.0C_4$	$0.0C_3$
Impurities, in bottoms, per cent	$0.0C_3$	$0.0C_4$	$0.2iC_5$	$0.3iC_4$
	......	......	......	$0.4C_5$
Number of trays	45	40	50	45
Height, ft	111	103	120	111
Diameter, ft	8.0	10.5	7.0	8.5
Safe working pressure, lb. per sq. in.	275	100	50	120
Reflux ratio (design figure)	12.8	2.6	15.5	10.3

Naphthas and Specialty Products.—The manufacture of narrow-boiling-range solvents is one of the most exacting operations that is carried out in the refinery. The boiling-range must be narrow, and the product must be well fractionated, but in addition the color must be excellent and stable with regard to light. No gum is tolerated, and the sulfur must be low. These requirements necessitate a thorough treating operation as well as careful fractionation. Most refiners do not manufacture solvents, and those who do are often secretive about the exact methods that they use.

In small refineries in which the shipments of solvents may not exceed a tank car per month, a common method of processing is to withdraw a small quantity of roughly cut material from the main distillation process and rerun this cut in a shellstill and tower, using a large quantity of reflux and conducting the distillation very slowly. In large refineries that specialize in the production of solvents, this method is unsuitable.

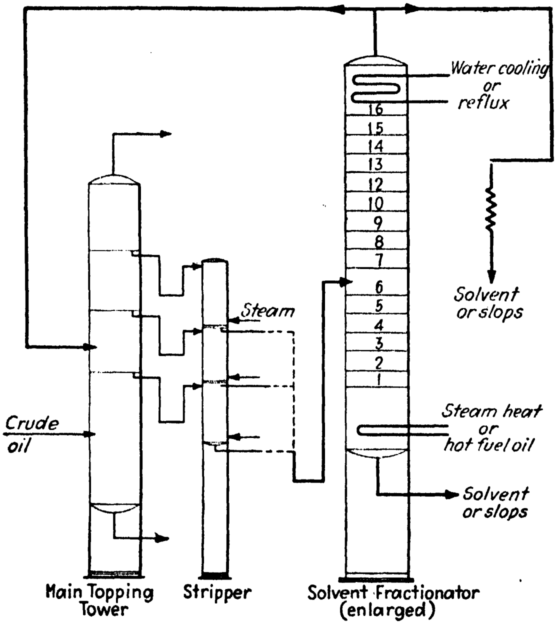

FIG. 110.—Diagram of solvent fractionator.

A product that is withdrawn from the side of a multiple-draw column can never be well fractionated. It will always contain some low-boiling material because the vapor that passes the draw-plate always contains the lighter products of the process. The end-point can be regulated to some extent by the use of many plates and large amounts of reflux, but a satisfactory initial boiling-point cannot be obtained by these methods. The regulation of the initial boiling-point is usually obtained by the use of a steam stripper. However, these common methods are ordinarily not satisfactory for the manufacture of solvents, and it is usually necessary to withdraw a partly fractionated material from the main tower and redistill this material under controlled conditions. Figure 110 indicates a flexible system that can be used in redistilling solvents. The auxiliary tower (enlarged in Fig. 110) is a rectifying and exhausting system having a reboiler that may be heated with high-pressure steam or by circulation of hot fuel oil from the main distillation unit. The system may be operated in many ways. The charge-stock may be drawn from any part of the main tower; the solvent may be either an overhead or a bottoms product; and in some cases it might even be advisable to collect it as a side-draw product from the auxiliary tower, although a side-draw connection is not shown in Fig. 110.

Pressed Distillate and Brightstock Solution.—The redistillation of pressed distillate in the manufacture of neutral oils must be conducted under vacuum or with the use of large amounts of steam. In other respects the equipment and method of operation are similar to those used in topping crude oil. Discoloration will result in a high treating cost, and hence the pipestill must be built with a large amount of radiant surface and for high oil velocities. Figure 111 shows a typical steam-atmospheric pressure distillate rerun plant, and Fig. 112 the evaluation curves of the stock.

The same equipment may be used to redistill brightstock solution, but, of course, a different quantity of material will be processed. The use of a single pipestill and fractionator system for several distillation operations is becoming a more and more common practice. By careful design a unit can be built that can be operated on either pressed distillate or brightstock solution. The unit is operated for several weeks on one of the stocks while the other stock is being accumulated in storage tanks. One small Pennsylvanian refiner is storing brightstock solution for about three weeks out of a month and processing it during the fourth week in the topping plant. It is reported that only 1 hr. is required to switch from the crude oil charging-stock to brightstock solution as the charging-stock.

Brightstock solution, like pressed distillate, must be distilled with as little discoloration as possible. Several two-flash systems

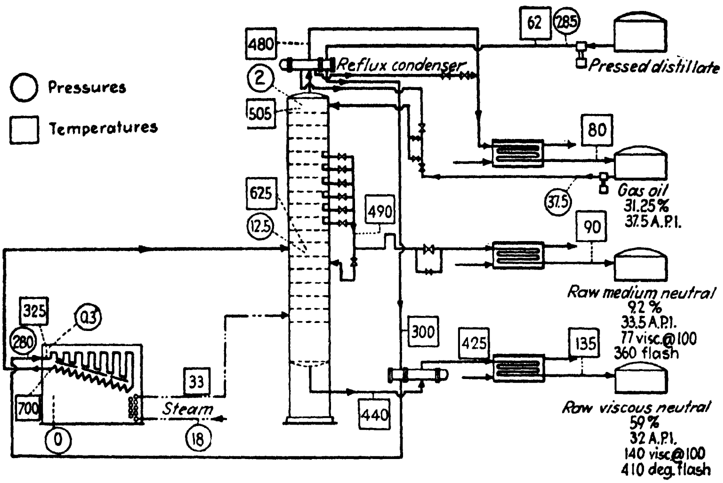

FIG. 111.—Diagram of a steam-atmospheric pressed-distillate rerun plant. (A stripper for the side product is generally used.) (*A. J. Smith Engineering Company.*)

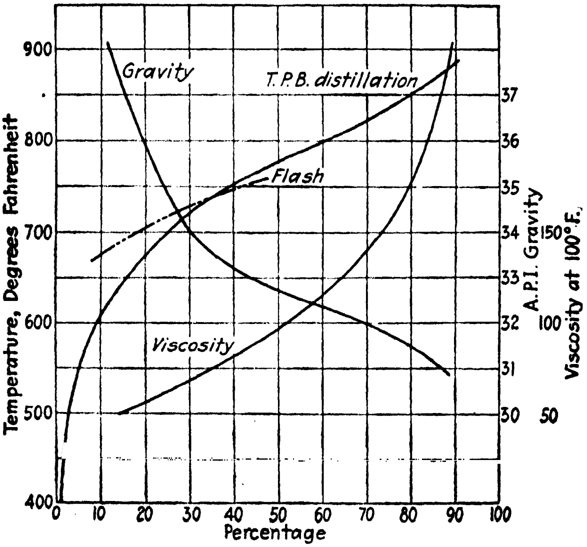

FIG. 112.—Evaluation curves of a pressed distillate.

have been built. In the first flash, the naphtha is removed. The residue is then further heated in a part of the pipestill, and gas oil

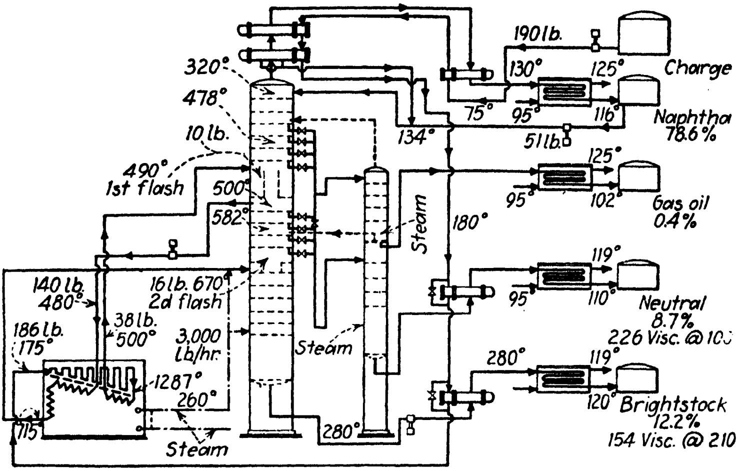

FIG. 113.—Diagram of two-flash solution rerun unit. (*A. J. Smith Engineering Company.*)

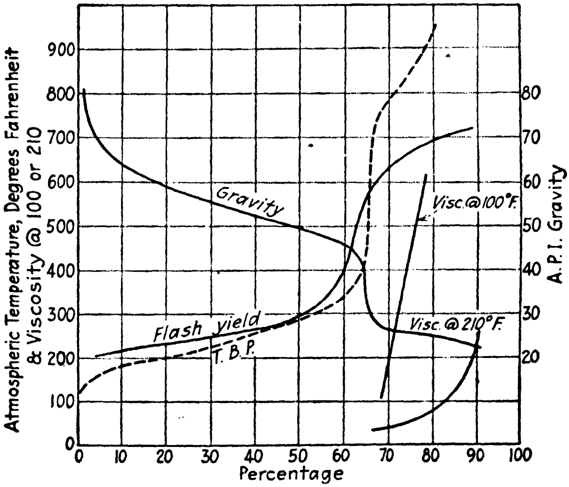

FIG. 114.—Evaluation curves of a brightstock solution.

and a neutral oil are vaporized in the second flash. The two-flash system holds no important advantages over the single-flash system, but as an illustration the two-flash method of operation is shown in Fig. 113. Evaluation curves are shown in Fig. 114. The steam required in a pipestill rerun system is often less than one-fifth the amount required by shellstill redistillation.

Steam Required for Stripping.—The amount of steam required for stripping side-draw and bottoms products cannot be a definite quantity. It will depend upon the flash-point that is required in the stripped product and upon the degree of fractionation that is obtained in the main tower. For ordinary conditions the following quantities of steam are recommended:

Material	Lb. Steam per Gal. Oil
Naphtha	0.1–0.2
Kerosene	0.2–0.3
Gas oil	0.3–0.6
Fuel oil	0.4–0.8
Pressure-distillate bottoms	0.6–1.0

If products of particularly high flash-point are required, then much larger quantities may be necessary. As an example, in a topping plant a 180°F. flash-point kerosene required 0.4 lb. of steam per gallon and a 280°F. flash-point gas oil required 2.25 lb. of steam per gallon.

Vacuum Distillation.—Vacuum distillation may be employed for the redistillation of pressure distillate, pressed distillate, or brightstock solution. It may be used for distilling topped crude oils for the production of wax distillate and cylinder stock, or it may be used to reduce a tar stock to asphalt or pitch. Vacuum systems have been used to produce gas oil (cracking-stock) from heavy tars.

The advantages of vacuum distillation for distilling asphalt-bearing crude oils is obvious, because the asphalt in such stocks makes the cost of acid treatment almost prohibitive. In the case of paraffin-base oils the advantages are not so obvious. The advantage with such oils lies in the larger recovery of the valuable heavy stocks, which in the case of residual steam operation are partly decomposed into lower boiling, less viscous oils.

Although the wax distillate and the cylinder stocks from vacuum units are usually dewaxed without difficulty, some refiners have found that an intermediate heavy wax distillate cut must be produced to the amount of 3 to 6 per cent if the wax distillate and the cylinder stock are to have good dewaxing characteristics.

Because of the high boiling-points of lubricating oil stocks the use of vacuum alone is not usually sufficient. Process steam must also be used and sometimes in such quantities as 1 lb. of steam for each gallon of reduced crude oil that is processed. Of course, the exact amount of steam to be used is dependent upon the boiling-range of the stock and the quantity vaporized. Many plants have operated with process steam not exceeding 0.3 lb. per gallon. The dry process of vacuum distillation, which utilizes no steam, has many theoretical advantages. Most important among these are the much smaller tower and condensing equipment required. Nevertheless, the absolute pressure that is required for the dry processing of most petroleum oils amounts to less than 1 mm., and such a vacuum cannot be produced at a reasonable cost in large-scale vacuum equipment.

The common method of maintaining a vacuum is by the use of a barometric condenser and steam jets. The steam and uncondensed gases pass into the barometric condenser. As the steam condenses, it shrinks greatly in volume and a vacuum is produced. The fixed gases cannot be condensed, and they must be ejected from the system by steam jets. By the use of a barometric condenser and steam jets, the lowest economical pressure that can be produced at the barometric is about 16 mm., and large amounts of steam and cooling water are required. Even this pressure cannot be obtained if the cooling water is above about 70°F.

To obtain lower pressures than 16 mm. or to obtain 16 mm. with normal cooling water, a thermocompresser or booster-ejector must be used. By the use of a barometric condenser, three stages of steam jets, and a booster-ejector, the low pressure of 8 mm. can be obtained (at the booster) if the water is cold. However, the steam consumption of a booster-ejector is very high, and it is not widely used. The booster-ejector is nothing more than a large steam jet that is used to compress not only the fixed gases but also the process steam. Thus the booster-ejector is used before the barometric condenser, whereas the regular steam jets are used to remove gas from the barometric condenser (Fig. 115).

The pressure-drop that occurs between the barometric condenser and the vaporizer section of the tower is of great importance. The purpose of vacuum operation is to produce a low effective pressure at the vaporizer, and hence the vacuum must not be lost by excessive friction loss through the vapor line, condensers, and tower plates. As an example, the following tabulation shows the pounds of process steam required at different effective vaporizer pressures. The table was computed for the processing of 1,500 bbl. per day of an average Mid-Continent reduced crude oil. The first column shows the pressure at the vaporizer; the second and third show the consumption of process steam at vaporizer temperatures of 680 and 700°F.; and the fourth column shows the approximate vaporizer temperature that is required if no process steam is used.

Operating pressure at vaporizer, mm. of mercury	Lb. of steam required per hr.		Temperature at vaporizer if no steam is used
	680°F.	700°F.	
760	54,000	38,200	980
100	6,480	4,420	810
50	2,880	1,850	765
40	2,160	1,340	752
30	1,440	822	740
25	1,080	565	728
20	720	308	720
18	575	206	712
16	432	103	703

Thus the avoidance of a few millimeters of pressure-drop, from the barometric to the vaporizer, is worth many pounds of process steam. The saving in the quantity of steam is important, but the reduction in tower size and the quantity of cooling water that is required are also worthy of note. From the tabulation it would appear that pressures of 25 to 30 mm. would be economical, but such is not always the case. In addition to the process steam as shown in the tabulation, steam is required to operate the steam jets and water is required to operate the barometric condenser. The steam requirement for the steam jets increases rapidly as the pressure is reduced so that the most economical vaporizer pressure often exceeds 30 mm.

In an effort to obtain a minimum pressure-drop, many novel arrangements and designs of vacuum-towers and condensing

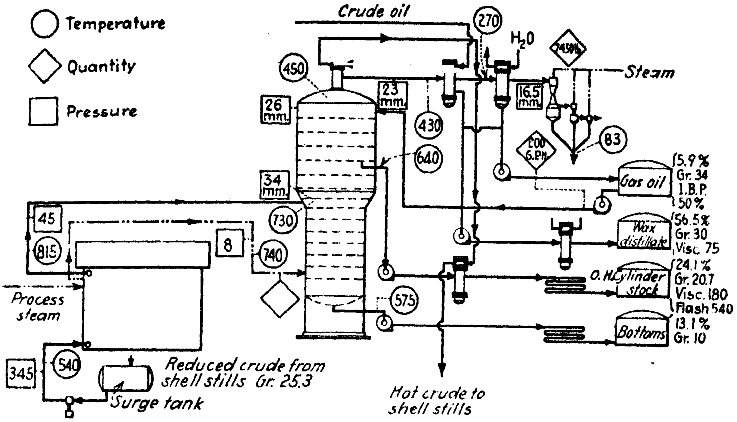

FIG. 115.—Vacuum distillation plant using a booster ejector. (*A. J. Smith Engineering Company.*)

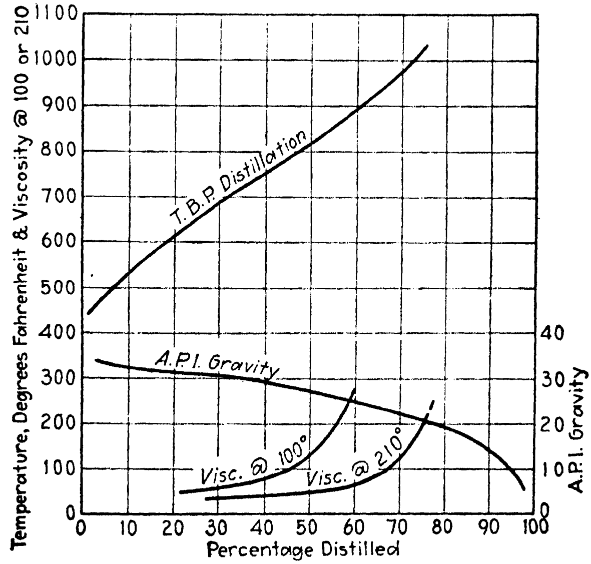

FIG. 116.—Evaluation curves for reduced crude oil charged to the plant shown in FIG. 115.

equipment have been developed. The plates are designed for as low a liquid head above the slots of the caps as possible, and sometimes the customary bubble caps are discarded entirely for baffle or splash types of plates. In some installations the vapor line has been eliminated by doing the condensing in the top of the tower. In this arrangement the barometric and jet equipment is situated along the side of the vacuum-tower (Fig. 117). The processing of a reduced crude oil in a vacuum unit for the production of distilled cylinder stock is illustrated in Figs. 115 and 116. In this plant a reflux condenser is placed in the top of the tower and the partial condensers for gas oil and wax distillate are outside the tower but not at a great distance. One of the difficulties with the arrangement shown in Fig. 115 is the weight of the large condensers. They are so heavy for a large installation that they cannot be supported by the tower. This necessitates independent structural supports and an elaborate expansion joint between the tower and condensers. Vacuum steam strippers are sometimes used on vacuum systems.

Fractionation is more effective at low temperatures or in a vacuum than at high temperatures. It is more effective because there is a larger difference among the vapor-pressures of the components at low pressures than at high pressures. Thus the relative tendency for propane to leave the liquid when at −50°F. is about four times as great as when the mixture is distilled at +50°F.. Perhaps this accounts in part for the relatively small number of plates that are used in vacuum towers.

VAPOR-PRESSURES, mm.

	−50°F.	0°F.	50°F.
Propane	630	1,913	4,395
Pentane	12	70	350
Ratio $\frac{\text{V.P. propane}}{\text{V.P. pentane}}$	52.5	27.3	12.5

Asphalt Plants.—The distillation of tarry residues in a vacuum, for the manufacture of asphalt, differs little in principle from the unit just described. The operation is simplified by the following factors:

1. Elaborate fractionation is not necessary. In the case of lubricating oil distillation, entrainment may discolor the products and increase the treating costs, and poor fractionation may result in trouble with dewaxing of both the wax distillate and the cylinder stock. Fewer plates are

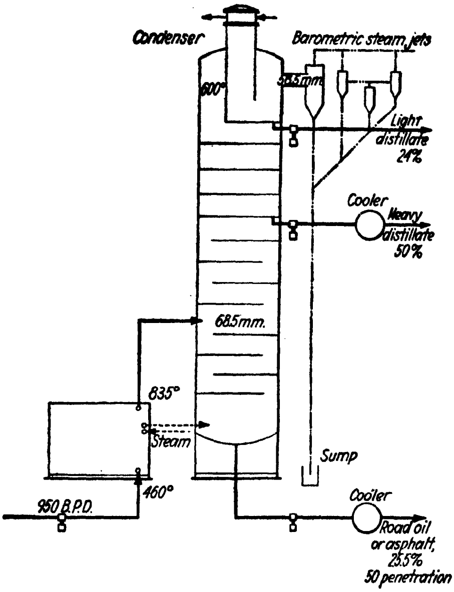

FIG. 117.—Vacuum flash system for asphalt manufacture.

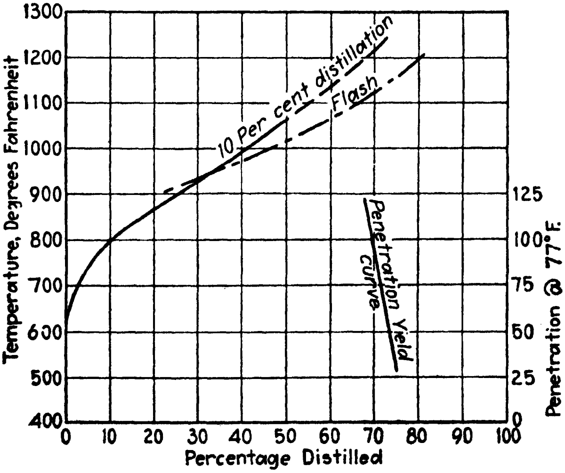

FIG. 118.—Charge-stock for unit shown in Fig. 117.

required in asphalt towers. Vacuum asphalt towers often have so few plates in them that they are referred to as flash jugs.

2. Higher vaporizer temperatures can be maintained without damage to the properties of the asphalt. Whereas the vaporizer temperature in lubricating oil towers is limited to a maximum of about 710°F., asphalt stocks are often heated to 790°F. without damage.
3. Only one product need be taken overhead. This eliminates the extra plates that are required for a side-draw cut or the partial condensers for two overhead cuts (Fig. 115). If two overhead cuts are taken, the separation is not difficult because both cuts are gas oils and they need not be well fractionated.
4. Tar stocks are usually available at a high temperature. A small heater is usually required, but in some cases a sufficient amount of vaporization occurs by simply reducing the pressure without the addition of heat.

A typical diagram, showing operating conditions, is given in Fig. 117. Evaluation curves are shown in Fig. 118. Note that the penetration yield curve is plotted differently from elsewhere in this chapter or in Chap. VII. Here the yields of asphalt are obtained by subtracting from 100 the value read from the curve. Thus, the yield of 100 penetration asphalt is about 30 per cent.

Similar but even more simple flash jugs are often used in cracking plants to reduce the cracked tar to a solid material and to obtain greater yields of gas oil for recycling.

CHAPTER XX

AUXILIARIES TO PROCESSING

Although the fundamentals of distillation processing were outlined in the preceding chapter, several auxiliary operations or equipments have been neglected. Only instrument control, crude oil desalting, and waste-water settlers will be discussed here. Refinery practice in the operation of boiler plants, water-cooling systems, piping systems, and pumping does not differ greatly from the standard practice in other industries.

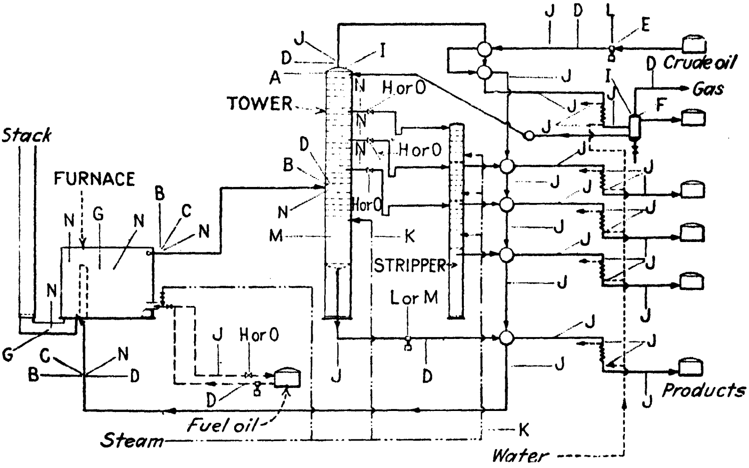

FIG. 119.—Instruments that may be used in a topping plant. The letters refer to the following instruments: *A*, temperature-recorder controller; *B*, recording pyrometer; *C*, recording pressure gage; *D*, indicating pressure gage; *E*, rate-of-flow controller; *F*, pressure regulator; *G*, draft gage; *H*, hand-control valve; *I*, safety valve; *M*, liquid-level control.

Optional instruments: *J*, industrial thermometers or thermocouple wells; *K*, flow meter; *L*, stroke regulator and counter; *N*, indicating thermocouples or connections for them; *O*, by-pass adjustment valves or proportional draw-off devices.

Instrument Control.—The full usefulness of refinery equipment can be attained only by the use of automatic and indicating control instruments. An attempt to discuss the merits of each individual instrument or type of instrument would be unsatisfactory because there are several different types of satisfactory instruments for each purpose and because radical improvements are being made each year.

Figure 119 indicates the location of the various control instruments that may be used in a topping plant. Many of these are optional, but all of those shown are in common use. Among the most important are (1) top temperature controller; (2) recording pyrometer at vaporizer and inlet and outlet of pipestill; (3) pressure at inlet and outlet of pipestill, at charge pump, and in tower; and (4) temperatures on side-draw plates. Control instruments are extensively used in natural-gasoline plants. Figure 120 illustrates the use of instruments in such a plant.

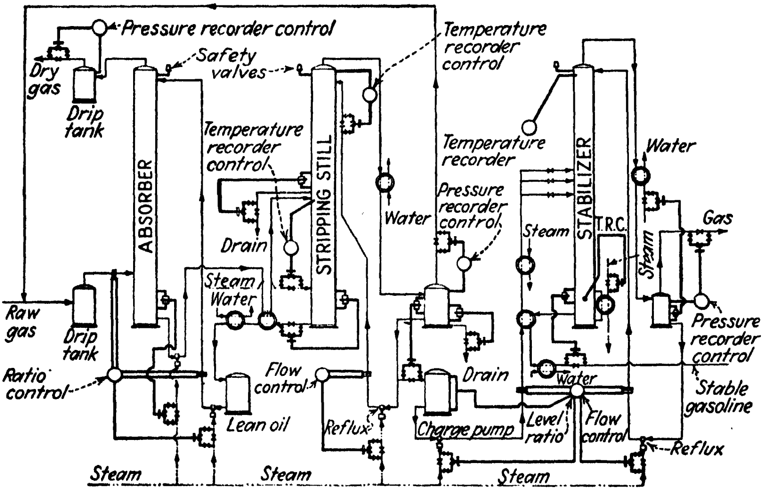

FIG. 120.—An extensive control system for a natural-gasoline plant.

In the control of a continuously operating system, certain variables must be fixed or the control of others is almost impossible. Of prime importance are (1) the rate of feed, (2) the temperature of feed, and (3) the top temperature of the tower. With these variables fixed, the control of the others is well within the capability of a competent operator. Even an expert operator is almost helpless if these three variables are not fixed. A plant can be operated with these controls alone, but the operation will be even more efficient if other controls are utilized. The rate of feed is commonly controlled by manual operation with the help of stroke regulators and stroke counters. The effect of a variable feed rate can be minimized by the use of proportional draw-off weirs.[1] The temperature of the feed normally gives little trouble, and several types of satisfactory top temperature controllers for towers are available.

The principle of trend-analyzing has been one of the notable improvements in instrument design. A trend-analyzing instrument is so constructed that it will begin to stop the actuating mechanism before the condition (temperature, pressure, or rate of flow) has been brought back to the desired condition. In this way the tendency to overcontrol, or "hunt," has been corrected. Such instruments apply a large correction if the condition is far from the control-point and a small correction (or none at all) if the condition is nearly at the control-point. This principle has been applied to many types of instruments, although not always under the name of trend-analyzer.

Centralized Control.—The central control room has become an integral part of the modern petroleum distillation unit. The grouping of recording and controlling instruments facilitates the work of the operator and concentrates the responsibility for the operation of the plant. Although the first cost of centralized and automatic control is high, it reduces the number of operators required to man the plant and provides an appreciable saving in operating cost. In dealing with emergency shut-downs, such as those arising from explosions and fires, the facility afforded by centralized control is of vital importance.

On the other hand, enthusiasm for the very real advantages of centralized control should not be allowed to obscure its limitations. Control instruments are expensive, and the lines between the control room and the equipment are costly. For this reason the less important measurements should be taken at the equipment, and indicating instruments should be given preference over recording instruments except where a record of the operating conditions is of definite service. A large number of instruments in the control room divides the attention of the operator, and hence careful thought should be given to the selection of the data that are to be presented for the attention of the control-room

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[1] CHILLAS and WEIR, *Ind. Eng. Chem.*, **22**, 206 (1930).

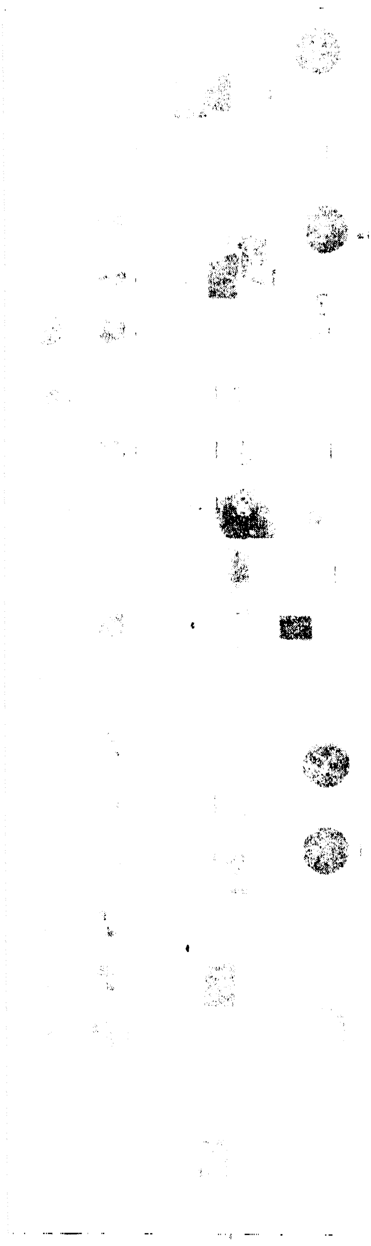

FIG. 121.—An elaborate instrument board used in controlling three pipestill distillation units. (*A. J. Smith Engineering Company.*)

operator. Figure 121 shows a single control board for three distillation units.

Desalting of Crude Oil.—The small amount of brine that is associated with crude oil is far more important than its quantity would indicate. In addition to the mechanical accumulation of debris in the processing equipment, the chloride salts (particularly magnesium chloride) liberate hydrochloric acid that causes corrosion during processing. This causes a decrease in heat-transfer rates by fouling, and promotes the formation of coke in the pipestill tubes. The removal of the brine often results in increasing the length of the operating cycle tenfold or more. Corrosion by hydrochloric acid is particularly troublesome if sulfide corrosion is also active, because the alloys used for one type of corrosion are not suited for withstanding the other type.

Brine is associated with crude oil both as a fine suspension of droplets and as more permanent emulsions. The demarcation line between these two types is not always clear; but the less-stable mixtures can be separated by simple settling methods, and the more permanent mixtures must be handled by chemical or electrical methods of separation. Long standing in storage tanks results in some settling—in one instance the salt content was decreased from 25 to 18.5 gr. per gallon by standing for 4 days. A high temperature is also useful, and the most common settling system consists simply of a horizontal tank operating at 100 to 400°F. and at sufficient pressure to suppress violent vaporization (50 to 250 lb. per square inch). The hot crude oil may also be sent through a vapor separator or evaporator prior to settling. The coalescence of particles is hastened also by the use of towers packed with sand (or gravel) or excelsior,[2] either before or after[3] the settling vessel. The time of settling may be cut in half by the use of a packed column of excelsior.[2] Water is usually mixed with the incoming crude oil. Union of the water with brine droplets is reported to be 75 per cent or more complete,[4] and hence the brine droplets that remain in the crude oil after settling contain very little salt.

[2] HAWTHORNE and BEDELL, The Removal of Inorganic Salts from Crude Petroleum, A.P.I., 8th Midyear Meeting, Wichita, Kans., May 24, 1938.

[3] BLAIR, C. M., JR., Removal of Inorganic Salts from Petroleum, *Oil Gas J.*, April 4, 1940, p. 52.

[4] EGLOFF, NELSON, MAXUTOV, and WIRTH, III, Crude Oil Desalting, A.I.M.E. Meeting, Oklahoma City, Oct. 8, 1937.

In simple heated settling tanks, a time of 1 hr. is common. The oil is introduced at one end of a horizontal settling vessel at a height about one-fourth from the bottom and aimed along the longitudinal axis of the vessel. The oil is removed in a similar manner at the top of the other end of the drum.

In handling more stable mixtures, the aforementioned simple heat- and water-diluent system may be assisted by the use of chemicals or a high-potential electric field across the settling vessel to cause more rapid coalescence of droplets. By these methods the salt content can usually be reduced by 90 per cent or more, and the time of settling may be reduced in some instances to only 20 min. Among the ingredients[5] of treating compounds are the following:

	Per Cent
Modified fatty acids partially or wholly saponified with ammonia	35–48
Oil-soluble sodium petroleum sulfonate	13–31
Water-soluble solvents, dilute alcohol (10–14 per cent), etc	10–20
Oil-soluble solvents, kerosene, crude oil, naphthas, cresol, etc	4–25
Inorganic sulfates, sodium sulfate, sodium sulfite	1–2

Few directions can be given for the selection of treating agents, but in general, for alkaline brines of high pH value the neutral soaps of oleic acid, solid fatty acids, liquid-saturated fatty acids, lincolic acid, etc., should be used;[6] for alkaline brines of lower pH ordinary turkey-red oil, with the sulfonate group esterified and loosely linked, may be successful; and finally, for more acid brines "one should consider the soaps of naphthenic acids, preferably having a low sulfate content, and the more stable fatty acid, alcoholic, or aromatic sulfonates, having a higher sulfate content, provided these are adapted to the pH of the water, and do not contain antagonistic constituents" (ones that cause precipitation). The use of small amounts of very dilute caustic soda solution (3 per cent of a 0.3 per cent solution) is found to be beneficial in some instances.[2]

Waste-water Disposal.—The pollution of streams and harbors by waste water from refineries has become a problem that must be met by all refiners.[7,8] Simple gravity type settlers are widely used. These function according to the basic law of Stokes:

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[5] BENNETT, H., The Chemical Formulary, Vol. 2, p. 179 (Tretolites), D. Van Nostrand Company, Inc., New York (1935).

[6] VAN DEDEM, G. W., Chemical Methods for Separating Petroleum Emulsions, *Oil Gas J.*, Aug. 12, 1937, p. 65.

$$v = 73.9D^2\left(\frac{s - s'}{z}\right)$$

where v = velocity of settling, ft. per sec.
D = diameter of particle, in.
s = density of particle, lb. per cu. ft.
s' = density of fluid, lb. per cu. ft.
z = viscosity of fluid, centipoises.

The law is not perfect, but it does constitute a guide by which the variables in empirical formulae such as the following can be ascertained. Babbitt and Schlentz[9] have developed this formula primarily from sewage-treatment tests. but it appears to be useful in designing oil-water settlers:

$$R = \frac{(D + 226)C}{3.72\left(C + \frac{216 - D}{4}\right)}; \qquad \text{or} \qquad D = \frac{3.72R(C + 54) - 226C}{C + 0.93R}$$

where R = percentage removal.
D = detention period, min.
C = concentration of oil at inlet, p.p.m.

Somewhat the same layout of settler as that developed by A.P.I. studies[7] is shown in Fig. 122. The flight scraper serves to move the sediments out of the box in a continuous manner. A filter[7] that utilizes cloth as the filter medium may be used after the settler for removing the last traces of iridescent oil film. Settlers are usually constructed of concrete and have a depth of 6 to 8 ft. Other dimensions are not of great significance provided the retention time is adequately long and provided the incoming waste water is evenly distributed across the settler. Many settlers are producing waste water that contains only 5 parts per million of oil. A film of oil ranging from 0.000006 to 0.000012 in. thick on the surface of water will produce an iridescent coloration.

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[7] HART, W. B., Elements of Waste-water Separator Design, A.P.I., 8th Midyear Meeting, Wichita, Kans., May 24, 1938.

[8] AMERICAN PETROLEUM INSTITUTE, Disposal of Refinery Wastes, Sec. I, 1933; Sec. II, 1938; and Sec. III, 1935.

[9] Results of Tests of Sewage Treatment, *Illinois Eng. Exp. Sta. Bull.* 198, 1929.

Separators cannot be expected to handle waters more highly acid than a pH of 4.5 or more alkaline than a pH of 10 or to handle true emulsions of oil in water such as so-called "white water." In such an emulsion the oil is dispersed through a continuous water phase and is carried through the separator. Later the emulsion may be destroyed by dilution or other effects that will liberate the oil. Emulsions of water-in-oil which may contain asphalt, clay, dirt, alkaline earth soaps, lead sulfide, or coke as the emulsifying agent are not usually troublesome. Occasionally, however, one of these emulsions will have a specific gravity that is the same as that of water, and it will not settle. All of these special cases should be met by corrections in the general processing scheme of the refinery rather than in the waste separator.

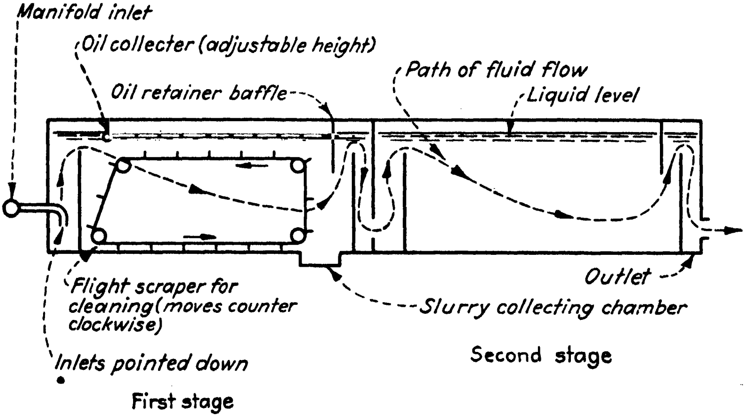
Manifold inlet
Oil collecter (adjustable height)
Oil retainer baffle
Path of fluid flow
Liquid level
Flight scraper for cleaning (moves counter clockwise)
Inlets pointed down
Outlet
Slurry collecting chamber
Second stage
First stage

FIG. 122.—Vertical section of waste-water separator.

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CHAPTER XXI

EXCHANGERS, COOLERS, CONDENSERS, AND STEAM HEATERS

The operation, maintenance, and design of heating equipment form an important part of the duties of the refinery engineer. Although most tubular equipment is designed and installed by manufacturing companies, under contract, the refinery engineer can hardly operate this equipment wisely or apply existing equipment to new uses without a clear understanding of the principles underlying their design.

The ultimate source of heat in the refinery is the steam boiler and the petroleum shell or pipestill. Indirectly, heat is obtained or saved from the various petroleum products by cooling them with the raw charging-stock. These products, at a high temperature, are passed through tubular equipments called heat exchangers, vapor heat exchangers, vapor condensers, or tubular coolers. If the two materials that exchange heat are liquids, the equipment is referred to as a *heat exchanger*. If the hot material is a vapor and is cooled without much condensation, the equipment is called a *vapor heat exchanger*. If the vapor is condensed, the equipment is called a condenser, and the equipment subsequently used to cool the condensate is usually referred to as a *cooler* or *after-cooler*. These cooling and condensing operations may be conducted in so-called *coil-in-box equipments*, although many refiners have discarded the coil-in-box arrangement except for particular services.

The large amount of water that is contained in coil-in-box equipment may be an advantage. Thus, if the water supply should fail, the run-down house will not be filled with uncondensed vapors with the attendant danger of a serious fire. In large refineries the water supply is unfailing and tubular equipment can be used with safety. In smaller refineries the danger has been largely eliminated by the use of oil as the cooling medium in at least part of the condensing system. During the last few years the design of tubular equipment has been so improved that it can be built as cheaply or even more cheaply than coil-in-box arrangements. Owing to higher velocities and the relative ease of cleaning, the heat-transfer rates in tubular equipment are usually more than twice as great as in coil-in-box equipment.

If the cooling water is very hard or dirty or if severe corrosive conditions exist, tubular equipment is usually not satisfactory. The scale that is produced is such a resistance to the flow of heat that the transfer rate in the tubular equipment may be scarcely larger than in coil-in-box equipment. Hence the advantages of tubular equipment are lost, and the cost of the installation mounts. The scale can be cleaned from the tubular equipment, but the scale may be deposited again so quickly, often after a few hours, that little is accomplished by the cleaning. Some refiners have found it necessary to return to the use of coil-in-box condensers and coolers. However, in many cases the apparent failure of tubular equipment to perform properly may be attributed to carelessness on the part of the refiner. Tubular equipment must be periodically cleaned or blown with steam, and those refiners who have followed this practice have usually found that the use of tubular equipment is economical.

The foregoing items are standard equipment. In addition, the *jet* type of *condenser* has been finding some application. The *barometric* jet-type condenser is now universally used in vacuum distillation to condense steam and at the same time create part of the vacuum. In this type of condenser, the vapor and the cooling medium are intimately mixed by high-pressure jets, and heat is exchanged by pure mixing or conduction. Theoretically, heat transfer by mixing is 100 per cent perfect and is the cheapest means of transferring heat. For ordinary condensation, jets have not been used extensively, perhaps because of the tendency of water to form emulsions with oil. The Fleming jet condenser (patented) is an example of the jet-type condenser, and almost all manufacturers build barometric condensers.

The use of *air-cooled condensers* and *partial condensers* for the separation of products that have different boiling-ranges has been discarded almost entirely in American practice. An exception is the use of partial condensers for the separation of wax distillate and gas oil in modern vacuum plants. In this case, the separation of wax distillate and gas oil is purposely not exact. Furthermore, partial condensers can easily be placed near the tower, and the more quickly the large volume of the vapor can be eliminated the less is the pressure-drop in the vapor line.

HEAT EXCHANGERS

Heat exchangers are built in a multitude of structural types. The primary aim in all of these designs is to obtain a high transfer rate without exceeding the allowable pressure-drop. Sometimes the pressure-drop is not important, as in pumping a charging-stock through a number of exchangers into a pipestill or in withdrawing hot liquids from a high-pressure process. However, very often the only pressure that is available with which to force the material through the exchangers and coolers is the static head of the fluid above the storage tank. Of course, pumps can be installed, but other factors such as the cost of power and the expense of upkeep, which are involved with all moving equipment, prohibit the use of pumps in many circumstances. In the rest of the chapter it will become apparent that an exchanger for a specific service can be built in a large number of ways. The liquid velocity may be varied on both sides of the heating surface, and various structural differences such as the type of shell-baffles, routing of the liquids, and other features, all have a definite effect on the over-all transfer rate and the pressure-drop. Some arrangements are less expensive than others, and it behooves the designer to find, or at least approach, the most economical combination of these factors.

Number of Passes.—In order to obtain a high velocity, it is usually necessary to arrange the flow of liquid through the tubes so that the fluid passes through one section of tubes and then returns through another section of tubes. As many as 16 sections or passes have been used. The same effect is produced on the outside of the tubes by means of baffles. In the past, exchangers have been built with as many as six liquid passes outside the tubes and even more passes within the tubes. Today, most manufacturers agree that two or at the most four passes of the liquid through the shell (shell-side of exchanger) are desirable and that multiple-passes of more than six on the tube-side are undesirable. If more passes are used, the conditions of true countercurrent flow cannot be attained and the mean temperature difference and total heat transferred may be decreased even though much higher shell and tube velocities are maintained. Occasionally, conditions are encountered in which crossing of the temperatures of the two liquids tends to occur. As exceptions, multiple tube-passes are an advantage if several exchangers are used in series and in the case of vapor condensers.

In an attempt to obtain true countercurrent flow, some refiners require single-pass exchangers for all services. In this extreme, the cost of several small shells, as against the cost of fewer large shells with several passes, is great, and particularly so if only a small amount of heat is transferred. From an operating standpoint the single-pass exchanger has many advantages and theoretically is the ideal arrangement. Some of these advantages are as follows:

1. Countercurrent flow is attained.
2. Cleaning is facilitated because one unit at a time can be removed from the system and cleaned without markedly interrupting continuous operation or changing the operating conditions.
3. For the same reason the repair of leaky tubes is facilitated.
4. Small tube bundles can be more easily removed and more easily flushed or cleaned.
5. Large multiple-pass units are bulky and cannot be easily installed and removed. In the case of vacuum partial condensers, the weight of the several units of condenser often amounts to over 50 tons. This great bulk at a height of 40 ft. or more is indeed awkward.

Countercurrent Flow.—One of the troublesome difficulties in heater design is to compute or estimate the average temperature difference that exists in multiple-pass exchangers. The most simple manner of approach is to compute the logarithmic mean temperature difference and apply correction factors. If a change of state occurs on either side of the exchanger, this method is not satisfactory and a more detailed method as explained under the heading of condensers should be used. As an approximation, fractions of the logarithmic mean temperature difference are suggested as shown in Table 53. These data were taken from the work of W. M. Nagle[1] and others.[2,3,4]

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[1] Mean Temperature Differences in Multipass Exchangers, *Ind. Eng. Chem.*, **25**, 604 (1933).

[2] Bowman, R. A., *Ind. Eng. Chem.*, **28**, 541 (1936).

[3] Fischer, F. K., *Ind. Eng. Chem.*, **30**, 377 (1938).

[4] Ten Broeck, H., *Ind. Eng. Chem.*, **30**, 1041 (1938).

$$R = \frac{T_1 - T_2}{t_2 - t_1}$$

where T_1 = temperature into shell, deg. F.
T_2 = temperature out of shell, deg. F.
t_1 = temperature into tubes, deg. F.
t_2 = temperature out of tubes, deg. F.

TABLE 53.—FRACTION OF MEAN TEMPERATURE DIFFERENCE ATTAINED IN MULTIPASS EXCHANGERS

$\frac{t_2 - t_1}{T_1 - t_1}$	Single-pass shell multipass tubes for these values of R					2-shell passes 4 or more tube passes for these values of R					4-shell passes 8 or more tube passes for these values of R				
	4	2	1	0.5	0.1	4	2	1	0.5	0.1	4	2	1	0.5	0.1
0.10	0.98	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.15	0.95	0.99													
0.20	0.83	0.97	....	......	....	0.96	....	......	....	....	1.0				
0.25	0.00	0.94	0.99	......	....	0.55	0.99	......	....	....	0.85				
0.30	....	0.88	0.97	......	....	0.00	0.97	......	....	....	0.00	1.0			
0.35	....	0.74	0.95	0.99	....	....	0.94	......	....	....	....	0.99			
0.40	....	0.00	0.92	0.98	....	....	0.88	0.99	....	....	....	0.98			
0.45	....	....	0.88	0.96	....	....	0.65	0.98	....	....	....	0.93			
0.50	....	....	0.80	0.94	....	....	0.45	0.96	0.99	....	....	0.45	1.0		
0.60	....	....	0.35	0.88	0.99	....	0.00	0.90	0.97	....	....	0.00	0.98		
0.70	....	....	0.00	0.73	0.98	....	....	0.71	0.94	....	....	....	0.94	0.99	
0.80	....	....	....	<0.30	0.94	....	....	<0.30	0.88	0.99	....	....	0.80	0.97	
0.90	....	....	....	0.00	0.85	....	....	0.00	0.62	0.97	....	....	0.00	0.93	1.0

Selection of Material through Tubes.—If one liquid is more viscous than the other, it should preferably be sent through the shell where turbulence can be obtained by the use of baffles. For the same friction loss, the over-all transfer rate is increased more than by sending the material through the tubes. If the volume of one liquid is much smaller than the volume of the other, the material should be sent through the shell and again by the use of close-spaced baffles a greater transfer of heat can be obtained with a minimum pressure loss. This is particularly true for the orifice-type baffles that will be discussed later. Very small tubes or a large number of passes would be required if the small volume were sent through the tubes, but neither of these two methods of increasing the rate of heat transfer is considered good practice.

The tubes of an exchanger can be easily built to withstand high pressures, and hence, if possible, fluids under high pressure are routed through the tubes. Shells are normally constructed of cast iron, and to build steel shells greatly increases the cost.

If coke or sediment may be deposited, the fluid should be sent through the tubes because they can be easily cleaned. Further, if the fluid is corrosive, special corrosion-resistant tubes can be obtained at a cost far below the cost of corrosion-resistant shells.

Obviously, materials that must occupy a large volume, such as gases or condensing vapor, should be routed through the shell so that structurally the passage can be large enough to avoid high velocities and prohibitive pressure-drops.

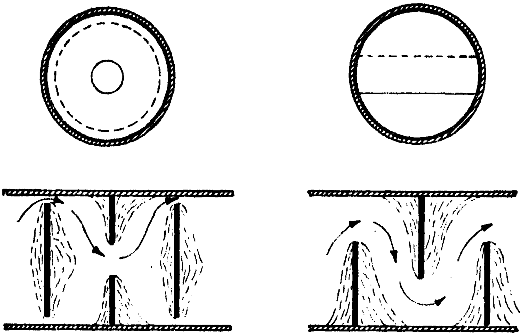
Water, used as the final cooling agent, is usually passed through the tubes because scale will be deposited and the tubes can be more easily cleaned.

Baffle Arrangements.—Baffles are widely used to increase the turbulence and film-transfer rate on the outside of the tubes. With the more widespread use of exchangers that have only a few passes on the tube-side, the baffle arrangements have become somewhat standardized. With multiple passes on the shell-side, the number of possible baffle arrangements becomes so large that they cannot be discussed, but for exchangers having only one or two passes on the shell-side the following standard baffle types are generally recognized:

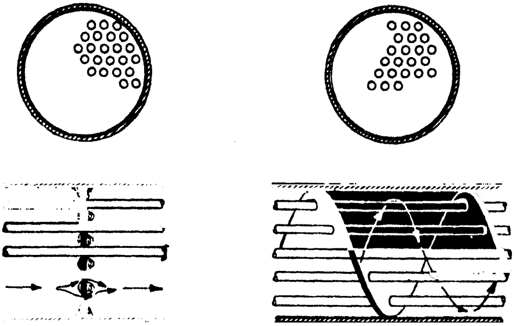
1. *Cross Flow. Alternate Circular Ports and Annular Spaces (Fig.* 123*a). Half-moon or Cutout (Fig.* 123*b*).—This type of baffle imparts a zigzag flow back and forth across the tubes. Obviously, dead-spaces cannot be avoided (Fig. 123*a* and *b*), but pressure-drops are comparatively low with this type of baffle. In general, this type is valuable for viscous fluids if only a small pressure-drop is permissible.

2. *Orifice (Fig.* 123*c*).—This type is built as oversize holes or ports through the baffle sheet. The tubes fit loosely in the holes, and the fluid is thus forced to scour the tube wall. Thus far, this type has proved to be one of the most effective means of increasing the film coefficient on the shell-side, but it has the disadvantage of causing a comparatively large pressure-drop. This type is particularly suited for use with light liquids under ordinary pressure heads.

3. *Spiral Flow* (*Fig.* 123*d*).—This type imparts a spiral flow to the fluid so that it crosses the tubes besides traveling longitudinally. The baffles are either continuous spirals or separate baffle plates, so placed that the liquid is directed into circular flow. The fluid suffers a friction loss by scouring the shell, and the turbulence created at the shell surface is not effective in causing heat transfer. In other words, the liquid tends to by-pass in the space nearest the shell and thus fails to transfer heat. The tube bundles must be easily removed, and hence the baffles must not fit the tubes closely. In this type a large amount of liquid fails to move spirally because of by-passing. This is not altogether a disadvantage because the baffle thus acts partly as an orifice baffle.



(a) Port and Annular Space (b) Half-Moon



(c) Orifice (d) Spiral Flow

FIG. 123.—Types of baffles for the shell side of small exchangers.

The closer the baffles are spaced the greater the turbulence and heat transfer. The pressure-drop increases at close spacings but not in proportion to the increased transfer rate. However, spacings of less than 6 in. are seldom used because of the difficulty encountered in cleaning the outside of the tubes. Exchangers in use today have spacings of 3 to 18 in.

Impingement baffles are placed at points that may be eroded by the velocity of the fluid. Usually these baffles are used only at the fluid entrance point, but at any point where the fluid suddenly changes direction impingement plates are recommended. Tubes in vapor condensers have been entirely severed by erosion in a few months of operation.

Longitudinal baffles are sometimes used, but their use is generally limited to vapor exchangers and condensers. In long small-diameter exchangers the longitudinal baffle provides too much area for by-passing and efficiency is sacrificed thereby.

If severe corrosion takes place on the shell-side or if the fluid contains large amounts of suspended matter, baffles may be a liability rather than an advantage. Removal of the baffles decreases the transfer rate, but a large amount of dirt in the stock may decrease the rate more than the removal of baffles. With no baffles the probability of plugging the shell-side is greatly decreased.

Tubes and Tube Spacing.—Tubes of 5/8 to 1½ in. outside diameter are used. In the past, ½- and 5/8-in.-diameter tubes were extensively used; but they often became plugged, and the outside could not be easily cleaned. Hence the use of ¾- and 1-in. tubes is now almost standard practice. For tubes above 1 in. in diameter, thicknesses of 10 to 16 B.w.g. are common, and for smaller sizes the thickness ranges from 12 to 18 B.w.g. Owing to the more vigorous cleaning methods that are now employed, the thicker tubes are more in demand.

The tubes are usually spaced at ¼ to 3/8 in. clear space from adjacent tubes and in an equilateral-triangle arrangement. Exchangers built with closer tube spacing are not accessible for cleaning. Later in the chapter the importance of frequent tube cleaning will be discussed. For severe fouling conditions, a square pitch arrangement with wide spacing is suggested, although for regular service the diamond or equilateral-triangle arrangement is the standard. A diamond pitch allows the tubes to be brushed on six sides.

Tubes are usually constructed of about 0.15 carbon steel, but in processing high-sulfur or salt-bearing crude oils, steel is rapidly destroyed by corrosion. For sulfur corrosion, 5 per cent chromium steel or 18-8 chrome-nickel tubes may be used. For acid corrosion, admiralty metal, a 70-29 brass containing 1 per cent tin, is recommended. Admiralty metal is slowly destroyed by dilute hydrochloric and sulfuric acid, but most of the neutralizers used for these acids do not act rapidly on it. Ammonia is the only one of the neutralizing agents that attacks admiralty metal rapidly. The mechanical properties of this alloy are impaired by temperatures above 500°F., although under favorable conditions it has been used at tube-wall temperatures of 600°F. Recommendations are as follows:

TABLE 54.—STANDARD CONDENSER TUBE DATA

O. D. of tube, in.	No. gage, B.w.g.	Weight per lin. ft., lb.	Thickness, in.	I. D., in.	Surface outside, sq. ft.		Surface inside per lin. ft., sq. ft.	Inside sectional area per tube, sq. in.	Velocity for 1 gal. per min., ft. per sec.
					Per lin. ft.	Per lin. in.			
⅝	14	0.520	0.083	0.459	0.16362	0.01364	0.1205	0.165	1.98
	16	0.421	0.065	0.495	0.16362	0.01364	0.1299	0.193	1.633
	18	0.326	0.049	0.527	0.16362	0.01364	0.1382	0.218	1.472
	20	0.238	0.035	0.555	0.16362	0.01364	0.1455	0.242	1.328
¾	14	0.64	0.083	0.584	0.19365	0.01637	0.1530	0.268	1.20
	16	0.514	0.065	0.620	0.19365	0.01637	0.1627	0.302	1.069
	18	0.396	0.049	0.652	0.19365	0.01637	0.1706	0.334	0.9617
1	12	1.12	0.109	0.782	0.26180	0.02179	0.205	0.479	0.67
	14	0.88	0.083	0.834	0.26180	0.02179	0.2183	0.5463	0.586
	16	0.700	0.065	0.870	0.26180	0.02179	0.2279	0.595	0.540
	18	0.540	0.049	0.902	0.26180	0.02179	0.2360	0.638	0.503
1¼	10	1.73	0.134	0.982	0.32708	0.02725	0.258	0.757	0.424
	12	1.44	0.109	1.032	0.32708	0.02725	0.271	0.838	0.385
	14	1.12	0.083	1.084	0.32708	0.02725	0.284	0.923	0.347
	16	0.890	0.065	1.120	0.32708	0.02725	0.2935	0.985	0.3262
	18	0.680	0.049	1.152	0.32708	0.02725	0.3020	1.045	0.3075
1½	10	2.110	0.134	1.232	0.3925	0.03275	0.3237	1.195	0.2688
	12	1.75	0.109	1.282	0.3925	0.03275	0.3382	1.292	0.2488
	14	1.36	0.083	1.334	0.3925	0.03275	0.3500	1.400	0.2298

Material	Highest working tube temperature, deg. F.	Max. temperature difference between adjacent tubes, deg. F.
Admiralty	450	145
Steel	500	130
Steel	800	95

In certain localities brackish cooling water cannot be avoided, and for such a service the tube sheets and if possible the shells should be constructed of the same material as the tubes, in order to avoid localized electrolytic corrosion.

Shells and Heads.—Most petroleum oil exchangers are of the floating-head type. As shown in Fig. 124, the tubes are free to expand and contract longitudinally by pushing the floating head back and forth within the shell. However, the head and tubes are not altogether free from stresses because the tubes that contain the hottest fluid expand more than the others. For this reason a number of floating heads in a single shell are sometimes employed. If the temperature difference between the two fluids is great or, in other words, a rapid rate of heat transfer occurs, two floating heads are advisable. This difficulty is sometimes avoided by the use of several small units of exchanger rather than one large exchanger with several floating heads. As an example, the hot vapors from a cracking plant evaporator are never cooled with crude oil or water at normal temperatures. The crude oil must be heated by other means to approximately 300°F. before sending it through the vapor condensers. Such condensers are usually built in several units. Too cold a medium (see tabula-

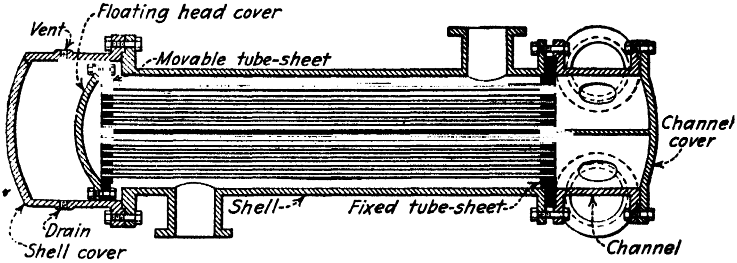


FIG. 124.—Double pass through tubes, floating-head-type exchanger. No baffles are shown on the outside of the tubes.

tion, page 397) may produce stresses and cause the tubes to fail. Tubes lighter than 12 B.w.g. tend to fail because the joint between them and the tube-sheet fails.

Cast-iron shells and heads should not be used at temperatures above 400°F. and pressures above 150 lb. per square inch. Below these maximum conditions, cast iron is to be preferred not alone because of cost but also because cast iron resists corrosion. Most active corrosion occurs during condensation of the vapor, and little action occurs after the material is completely condensed. At higher temperatures and pressures, cast-, forged-, or welded-steel shells are used. Cast steel is not an entirely homogeneous material, and sometimes the manufacturer must make several of these large and expensive castings before a satisfactory shell or head is obtained. Forged-steel shells are expensive, but when properly manufactured they can be used safely up to pressures of 1,000 lb. per square inch and at a temperature of 700°F. Recently the art of welding has been so improved that shells and particularly heads are now manufactured by machining and welding heavy plate steel. This method seems to be among the best for very high-temperature high-pressure equipment, and the cost is about equal to that of forged-steel construction.

FILM TRANSFER RATES

The film rates presented in this chapter are based primarily on the equations given in Chap. XIII. However, the equations are for clean surfaces that in some cases had been polished, and hence the values of the film rates had to be decreased in order to represent commercial conditions. The magnitude of the correction was estimated by a study of observed transfer rates in new, clean commercial equipment. In some cases approximations were necessary because of inadequate data, and in others it was necessary to simplify the cumbersome equations so that the film rates could be presented in a usable form.

The over-all rates obtained by the film rates given herein are far too high for most commercial equipment, and the *fouling factors* that are given in Fig. 128 *must be used.* Unfortunately, plant men have made no determined effort to catalogue fouling factors. This lack of information has led many engineers to attempt to correlate transfer rates without isolating a factor to care for the surface condition, and these efforts have been without success.

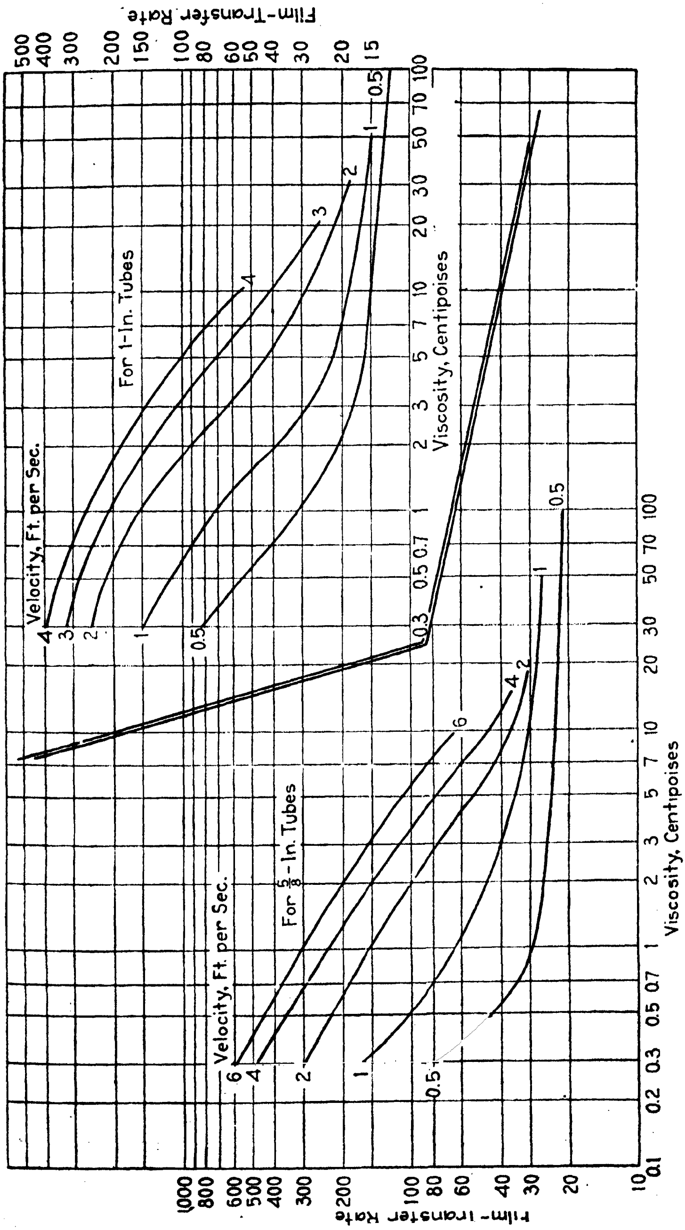


FIG. 125.—Approximate film transfer rates for oils inside of 5/8- and 1-in. tubing. A fouling factor must be applied to these rates.

When the transfer rates and fouling factors that are given in this chapter are used, the computed rates check reasonably well with commercial exchanger data. However, the method of evaluating fouling factors and dirtiness resistances, as given in the chapter, is by no means a finished correlation.

In order to get the high rates given in Chap. XIII, it is usually necessary to clean all scale from the surface and remove the dirt and grease that always accumulate during handling, and in some cases the surface must be polished or cleaned with chemical solutions.

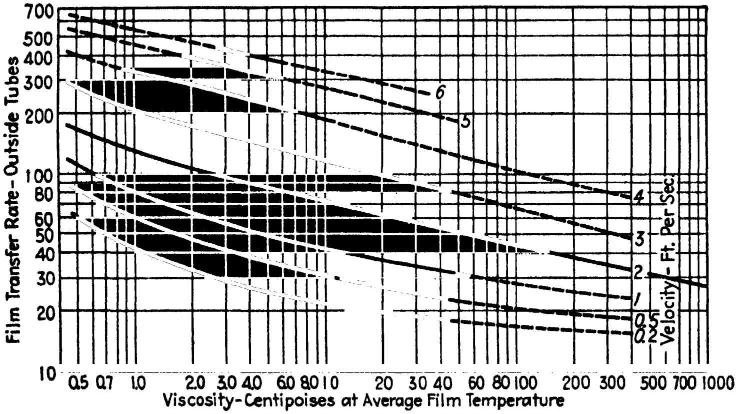


FIG. 126.—Approximate film transfer rates for oils on the outside of tubes in tubular-type equipment. These rates will vary with different types of shell baffles. Fouling factors must be used with these rates.

Liquid Film Coefficients.—Figure 125 shows the film coefficients for oils flowing in $\frac{5}{8}$- and 1-in. tubing. No correction for turbulence at the ends of the tubes need be applied. The size of tube has little effect if the viscosity is low; but if the viscosity is high, the size of tube is very important. If large film temperature differences exist (see page 206), the viscosity at the mean film temperature should be used; otherwise the viscosity at the main body temperature of the fluid may be used without introducing serious errors.

Figure 126 shows the magnitude of film coefficients for oils flowing on the outside of tubes. Owing to the many types of baffles and many possible arrangements, these shell-side rates cannot be exact for all exchangers. The velocity referred to in

Fig. 126 is the mean resultant velocity of the fluid through the shell and baffles and between tubes.

The film-transfer rates and fouling factors presented in this chapter have been checked against the commercial operation of 75 exchanger installations,[5] which include nearly all types of equipment. Although the average percentage error of the computed transfer rates as compared to the actual rates is only +4.25 per cent, 30 of the computed rates were low by an average of 10.4 per cent and 45 were high by an average of 11.2 per cent. In a few instances, primarily in light oil condensers and coolers, the percentage error in the computed transfer rate exceeded 25 per cent and in one instance was 87 per cent high.[6] Light oil equipment is most difficult to handle because of the presence of steam and gases and because the degree of fouling cannot be accurately estimated. By leaving out the 8 exchangers that

TABLE 55.—TRANSFER RATES FOR WATER

Velocity	Rate		Notes
	Inside	Outside	
...	...	50	Natural-convection, pipe coil (small equipment)
...	...	110	Natural-convection, ribbed sections (small equipment)
0.5	180	170	Natural-convection (commercial), small temperature difference
1.0	230	200	Natural-convection outside coils (commercial conditions)
2.0	350	280	Forced circulation
4.0	560	400	Forced circulation
6.0	660	500	Forced circulation

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[5] NELSON, W. L., *Oil Gas J.*, Jan. 19, 1939, p. 40; and July 4, 1940, p. 32.

[6] To the novice or to the scientist, these variations may appear to be excessive. It might be pointed out, however, that the source of most of the data studied in Reference 5 was studies of commercial installations that had failed to meet the guarantees of the equipment manufacturers. In most instances the guaranteed rate was high by 10 to 100 per cent. In the opinion of the author, these discrepancies are due primarily to a lack of cleanliness in refining operations and to failure on the part of manufacturers to design for long-time operation rather than for the initial operation under clean conditions.

showed an error over 25 per cent, the average percentage error is zero and the average deviation plus and minus is −9.4 and +6.25.

Table 55 summarizes the water film coefficients for coolers and condensers operating at normal water and oil temperatures.

F. L. Kallam[7] has studied the film transfer rate on the outside of tubes that are being cooled with water when the water drips or is sprayed on the tubes. He recommends the following equation for the water film coefficient for the outside of tubes:

$$h_o = 190N^{0.05}\left[\frac{W^{0.3}(P - D)^2}{2.42ZVP}\right]^{4.4} \tag{76}$$

where N = number of tube-rows high.
G = weight of spray water that strikes cooling surface, lb. per hr.
L = length of tubes exposed to water, ft.
B = width of tube bundle exposed to water, ft.
D = outside diameter of tubes, ft.
Z = absolute viscosity of spray water at logarithmic mean temperature of water on and off cooling surface, centipoises.
P = tube spacing in horizontal plane, ft.
V = vertical distance between tubes, ft.
$W = G/LB$

Fouling factors must be applied to the rates by this equation.

Velocity on the Outside of Tubes.—Fundamentally, the velocity in the tubes and in the shell is dependent upon the pressure-drop that can be permitted. However, the computation of pressure-drop is so complicated, particularly on the shell-side, that pressure-drop cannot be used as the logical basis of design. The computation or estimation of the velocity on the shell-side is also difficult. The following derivation for an exchanger having one pass through the shell illustrates how the velocity on the shell-side can be estimated:

Let n = number of baffles.
x = distance between baffles, in.
D = diameter of exchanger, ft.
L = length of exchanger, ft.
N = number of tubes.
d = diameter of tubes, ft.

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[7] KALLAM, F. L., private communication to the author, 1939.

h = height of baffle, ft.
F = volume of feed, cu. ft. per sec.
V = velocity, ft. per sec.

Approximate average distance of travel:

$$\text{Travel} = L + \frac{nh}{0.707}$$

The 0.707 factor corrects for the 45-deg. cross flow of the liquid as it travels between tubes spaced in an equilateral-triangle arrangement. At very low velocities the travel more nearly equals $(L + nh)$ divided by 0.707.

The time in the exchanger is a constant that is equal to the net internal volume between the shell and the tubes, divided by the volume of the feed.

$$\text{Time} = \frac{0.785L(D^2 - Nd^2)}{F}$$

$$V = \frac{\text{travel}}{\text{time}} = \frac{(L + 1.41nh)F}{0.785L(D^2 - Nd^2)}$$

or

$$n = \frac{0.785VL(D^2 - Nd^2) - LF}{1.41Fh}$$

The spacing of the baffles may be computed for a known velocity and tube arrangement by noting that

$$x = \frac{12L}{n}$$

or

$$x = \frac{16.9hF}{0.785V(D^2 - Nd^2) - F}$$

Similar derivations can be prepared for multipass shells. The main inaccuracy of such derivations lies in the fact that certain parts of the path of liquid flow remain almost stagnant whereas the velocity is high at other parts and that leakage occurs past the baffles. To some extent, however, the low- and high-velocity areas tend to counterbalance one another, and the leakage past the baffle is at such proximity to the heat-exchange surface that it may increase the rate of transfer in spite of the lower velocity. Similar equations of average velocity have been used by Short, Stack, and Perrone.[8]

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[8] SHORT and STACK, *Oil Gas J.*, May 10, 1934, p. 115; and PERRONE, S. A., *Oil Gas J.*, Mar. 28, 1935, p. 71.

In general, for cross-flow baffles on the shell-side and when the same volume of liquid is handled through the shell and through the tubes, the following approximate velocities will result:

	Tube passes	Velocity in	
		Tubes	Shell
No cross baffles	1	1	0.2–0.4
No cross baffles	2	1	0.1–0.2
Normal cross baffles	2	1	1.5–3.0
Large number of baffles	2	1	2.5–5.0

For other than a 1:1 ratio of fluids, the preceding approximate velocities can be corrected by simple arithmetic ratios.

Condensing Petroleum Vapors.—Many factors are involved in the film condensation coefficient of vapors and mixtures of vapor and noncondensible gases. In addition to the common variables (Chap. XIII), the latent heat and the temperature difference across the film are significant. Equations for condensation coefficients have been studied by several investigators,[9,10] and these references must be consulted for experimental or theoretical studies. For most commercial work the rates given in Table 56 are satisfactory.

TABLE 56.—FILM COEFFICIENTS, CONDENSING

Material	B.t.u./(deg. F. diff.)(sq. ft.)(hr.)	
	No steam	With steam, but steam not condensing in same temperature range as vapor
Natural gasoline	210–250	170–210
Gasoline	180–220	130–170
Kerosene	150–190	100–120
Gas oil	130–180	60– 70
Wax distillate	110–160	50– 60

If steam condenses with the vapor, an average coefficient can be computed[10] by determining the condensation coefficient for

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[9] McADAMS, W. H., "Heat Transmission," p. 256, McGraw-Hill Book Company, Inc., 1933.

[10] KIRKBRIDE, C. G., *Ind. Eng. Chem.*, **25**, 1324 (1933).

each of the pure materials and then combining the two coefficients in proportion to the amount of heat that is delivered from each material. Kirkbride[10] also discusses the effect of permanent gases on the condensation coefficient.

The variation in the coefficients found in Table 56 is due mainly to the temperature difference across the film. If the temperature difference is large, the rate is low; and if it is small, the rate is high. This is due to the accumulation of a thick film of liquid at high rates of condensation. In parts of the condenser in which no vapor remains and liquid stands about the tubes, the transfer rate is very low and probably does not amount to more than 30 to 50.

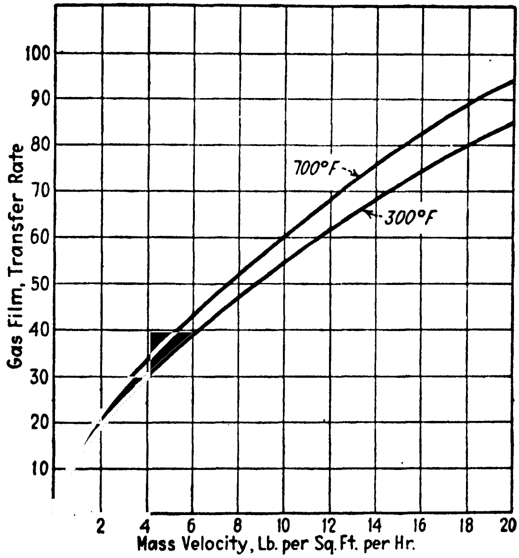

FIG. 127.—Film transfer rates for cooling or heating gases and vapors on the outside of tubes. A fouling factor must be applied.

Pure steam condenses at a rate of about 2,500, but in the presence of liquids and small amounts of vapor, as in a distillate condenser, the rate probably does not exceed 400.

Cooling Vapors without Condensation.—Scattered data on commercial vapor coolers indicate that the film rates are somewhat as shown in Fig. 127. The mass velocity that is used as one axis in this figure can be most easily computed by multiplying the linear velocity, in feet per second, by the density expressed as pounds per cubic foot. It may be visualized as the pounds of material that passes a square foot of free cross section per second.

FOULING FACTORS

Most of the difficulties that arise in heat-exchanger design and operation are due to an inadequate knowledge of the fouling of the surfaces of the equipment. Except under special conditions the effect of these fouling resistances can never be exactly known. If the stocks are exceptionally clean, if the equipment is periodically cleaned, or if the condition may be carefully studied in the plant for several months, then it is possible to foretell with fair accuracy the magnitude of the fouling factor.

In order thoroughly to understand fouling, it is necessary to compute film temperatures, wall temperatures, etc. These may be computed by means of the following equation:

$$\Delta T : \Delta T_1 : \Delta T_2 : \Delta T_f : \text{etc.} = \frac{1}{H} : \frac{1}{h_1} : \frac{1}{h_2} : R_f : \text{etc.} \qquad (77)$$

Difficulties arise in applying the equation because the film transfer rates are not usually known until the temperature differences are computed. This necessitates a trial-and-error solution to determine the film rates and the temperature differences at the same time.

The great lowering of clean film rates by fouling has often led plant engineers to believe that something must be wrong with the film rates that have been published. As an example, two exchangers operate under such conditions that the over-all rates computed by the film coefficients are 125 and 25. If both exchangers become fouled by the same amount, *i.e.*, a fouling resistance of, say, 0.02, the over-all rates drop to 36 and 17 respectively. The decrease in transfer rate is so large in the first exchanger and so little in the second that naturally the plant engineer felt that something must be wrong.

The resistance due to fouling is often so small that the position of the decimal point may become confusing. Hence the use of the term fouling factor has become common. The *fouling factor* is obtained by multiplying the fouling resistance by 1,000. Thus, if the fouling resistance is 0.005, the fouling factor is 5.

Classification of Fouling Conditions.—Although there are many individual conditions of fouling, all of them can be generally classified as follows:

1. ***Hard Deposits.***—Examples of this type of fouling are water scale, corrosion scales, rust, and hard coke. In general, the thickness and resistance of these deposits increase with time and nearly directly proportional to time. They cannot be effectively removed by blowing with steam or by flushing with hot water, but some of them can be removed by the use of chemicals. The chemical solution may be pumped through the equipment, but sometimes the tube bundle is removed and dipped into a vat that contains the chemical.[11] The usual manner of removing hard deposits is by the use of cleaning tools and brushes. The resistance offered by hard, dense deposits is directly related to the conductivity of the material composing the scale.

The rate at which fouling occurred in a particular naphtha condenser, cooled with water, is given by Samans.[12] The decrease in rate and the corresponding fouling factors are given in Table 57.

TABLE 57.—FOULING OF A NAPHTHA CONDENSER

Days	Not cleaned		Blown with steam, and blown daily after 18th day	
	Transfer rate	Fouling factor	Transfer rate	Fouling factor
1	50	0	50	0
2	44	2.7		
4	40	5.0		
6	37.5	6.7		
10	33	10.3		
14	29.4	14.1		
20	....	....	34	9.4
30	....	....	32.4	11.0
50	....	....	30.0	13.5

In another naphtha condenser (water cooled) the following data were recorded:

Days after Cleaning	Transfer Rate
2	39
4	33.2
7 and 8	28.7

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[11] ANON., Cleaning Refinery and Gasoline Equipment, *Ref. Nat. Gaso. Mfr.*, August, 1933, p. 340.

[12] A.S.M.E. Section Meeting, May, 1933.

2. *Porous Deposits.*—These deposits often consist of essentially the same materials that compose the hard deposits. In addition, coke or carbon may be deposited from fluids such as topping-still bottoms, asphalt or tar from vacuum plants, or cracking-still bottoms. Scale-forming mud and dirt may be deposited from water or from crude oil. Frequently the scales caused by corrosion are porous but not loose enough to be removed by blowing with steam. These deposits may be more serious than hard scales because the fluid contained in the porous material usually has a lower conductivity than the hard skeleton of the scale, and thus the over-all conductivity is low.

Sieder[13] presents data showing the rate at which one type of porous deposit was accumulated. An evaporator was operated with steam on the outside of the tube bundle, and a mixture of oil and water containing lint, in the tubes. The lint was deposited at a rate directly proportional to time. At 13 hr. the fouling factor was about 2; and if the deposit had continued to grow at the same rate, it would have caused a factor of 20 in about 5½ days. However, it is not to be inferred that porous scales are deposited at a rate directly proportional to time. The deposit described by Sieder might dislodge itself after attaining a greater thickness and hence might properly be classed as a loose deposit. Both the hard and the porous deposits can be removed to some extent by the use of bent-tube sections. These sections consist of a bank of condenser tubes (usually in an open box) which are bowed slightly during manufacture so that as heating and cooling occurs, they bend and cause the scale to loosen.

3. *Loose Deposits.*—Examples of this type of deposit are silt, mud, soot, powdered coke, leaves, or vegetable fiber. Many of these can be removed by swabs or brushes, and some can be effectively removed by blowing with steam or air or by flushing with hot water. The resistance caused by these deposits is not greatly dependent on the material composing the deposits but rather upon the liquid that is trapped within them. As far as decreasing the rate of transfer is concerned, loose deposits may be more effective than other types. Hard scales, and sometimes porous deposits, are usually so tightly fastened to the surface that they are affected little by a high velocity, but many loose deposits can be almost completely removed by maintaining a velocity higher than 4 ft. per second.

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[13] *Oil Gas J.*, May 10, 1934, p. 104.

The effect of blowing with steam, even for a fairly tight scale, is illustrated in Table 57. The condenser showed a better rate at 50 days, when blown with steam, than it did at 14 days if no blowing was practiced.

Fouling factors can be computed from the thickness of the scale of dirt if the thermal conductivity of the deposit is known. Not much information on the conductivity of scale materials has been recorded because of the great variation in types and densities of deposits. Some information from the Tubular Exchanger Manufacturing Association[14] and other references[15] is shown in Table 58.

TABLE 58.—THERMAL CONDUCTIVITY OF REFINERY SOLIDS

Material	Condition	Conductivity, B.t.u. × ft./(deg. F.)(sq. ft.)(hr.)
1. Carbon.............	Lampblack	0.038
2. Carbon.............	Graphite-compressed powder (passes 100 mesh)	0.103
3. Carbon.............	Coke-solid	0.476
4. Carbon.............	Amorphous	2.46
5. Carbon.............	Diamond	75.00
6. Carbon.............	Cracking coil coke	3.25
7. Soil................	Wet	0.386
8. Soil................	Dry	0.075
9. Portland cement....	....	0.173
10. Iron sulfide.........	....	4.1
11. Lube...............	Refined	0.083
12. Asphalt............	No mineral aggregate	0.097
13. Road asphalt.......	....	0.425
14. Paraffin wax........	....	0.136
15. Boiler scale.........	An average of many tests	1.43

Commercial Fouling Factors.—The magnitude of commercial factors can be best approached by means of a chart.[16] Figure 128 shows factors that were obtained in commercial equipment. The lines in the figure are merely boundaries of the several conditions of fouling. It would be more convenient to draw average curves for each condition, but to draw such a definite relation would be misleading. The desire of every engineer is to have definite fouling factors so that the responsibility can thus be lifted from his shoulders. This would be a restful solution to this troublesome problem, but such a solution will probably never be possible. Each condition of fouling is a new condition and can be met only by the judgment of the designer.

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[14] Standards, Tubular Exchanger Section, 366 Madison Avenue, New York, N. Y.

[15] NELSON, W. L., Fouling of Heat Exchangers, *Ref. Nat. Gaso. Mfr.*, July, 1934, p. 271.

[16] NELSON, W. L., Fouling Factors in Heat Transfer Equipment, *Ref. Nat. Gaso. Mfr.*, August, 1934, p. 292.

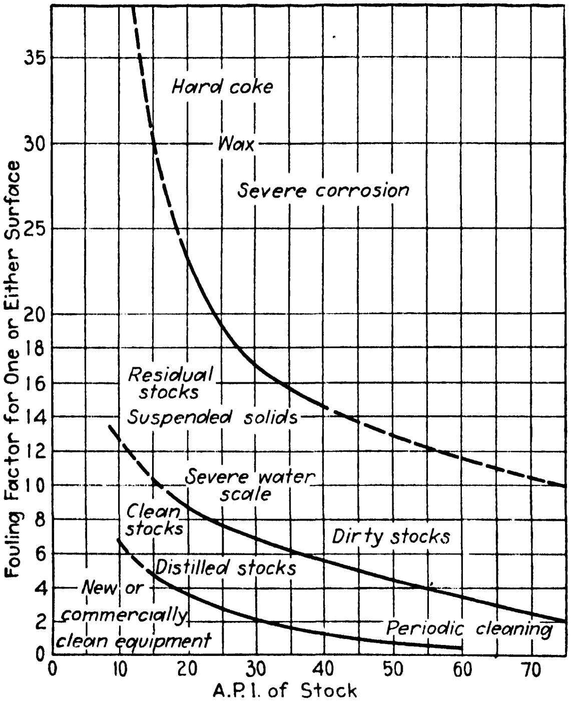

Fig. 128.—Approximate fouling factors for oils in commercial equipment. This chart shows the individual factors for each side of a surface, and hence, in the usual case, two factors must be added together to obtain the total fouling factor.

The lowest area in Fig. 128 is hardly applicable to any commercial situations except perhaps distilled water or other filtered clean stocks. The next higher area applies to well-serviced equipment operating on commercially clean stocks, and the factors shown would generally be considered as minimum commercial fouling factors. The next area shows factors that unfortunately apply in many refineries or in situations in which the equipment is not cleaned except at shut-down periods. The upper area involves such conditions that heat-exchange is not economical but may be unavoidable as in cooling wax-stocks or heating oils in pipestill tubes.

TABLE 59.—MISCELLANEOUS FOULING FACTORS

	Fouling Factor
Gases:	
Steam	none
Steam (exhaust)	5
Vapors, refinery	3–6
Vapors from cracking evaporator	6–10
Natural gas and air	1.5–4
Commercial oils:	
Fuel oil	0.5–1
Lube, recirculated	1–3
Quenching oils	4–6
Asphalts and resins	10–15
Water:	
Refrigeration brine	1–2
Sea water	0.5–3
Brackish water	1–4
Muddy or silty water	2–8
Spray pond water, untreated	3–8
Open type cooler water	2–7
City or well water (as Great Lakes)	1–3
Hard (over 15 gr. per gal.)	3–7
Treated boiler feed water	0.5–3
River water, minimum	1–3
River water, Miss., Del., River water, Schuylkill, East River, and New York Bay	2–5
River water, Chicago Sanitary Canal	6–13
Gasoline plants and debutanizer:	
Gases	0.5–2
Absorption oils	1–5
Gasoline	0.5–1
Solvent plants, treating and dewaxing:	
Feeds	1–3
Solvents	1–2
Gums, asphalts, resins, etc	10–20
Oil-wax cooling	3–20

The fouling factors given in Fig. 128 are for one surface only; *i.e.*, two factors must be obtained, and the sum of the two is the total fouling factor. It is difficult to isolate the fouling factor for each side of the surface, but to isolate the factors does allow the application of judgment in a sound manner. The fouling factor may be estimated as follows:

An exchanger is to cool a clean wax distillate (480 to 280°F.) in the tubes (3.7 ft. per second) by means of crude oil. The crude oil is heated (160 to 230°F.) on the outside of the tubes (1.8 ft. per second). The exchanger will be blown with steam once a week. The factor for the tube-side will be about 3 because the stock is clean and the velocity is fairly high. The factor for the shell-side will be about 4 because the velocity is high and the crude oil does not contain a large amount of dirt. Both of these factors are lower than normal because of periodic cleaning with steam. The total factor will be about 7. If the exchanger were not blown with steam, the factor might be 10 or 11. If the wax distillate were cooled with water, a wax film would be produced and the total factor might be 25 or even higher.

The fouling factors shown in Fig. 128 are for liquid petroleum oils. Vapor, water, and special situations cannot be plotted on such a diagram, and hence Table 59 from the Tubular Exchanger Manufacturing Association,[14] Kallam,[8] and personal data of the author is suggested.

Example 62. Transfer Rate for Exchanger.—Kerosene is to be cooled from 400 to 300°F. by means of 35 A.P.I. crude oil. The crude oil rises in temperature from 270 to 285°F. The exchanger has ⅝-in. tubes. The crude oil is relatively clean so that little dirt settles from it, and the exchanger will be blown with steam each month. The conditions are as follows:

Place	Material	Viscosity, centipoises	Approx. film temp., deg. F.	Velocity	No. passes
Shell	Crude oil	0.6	280	1.5	2
Tubes	Kerosene	0.3	340	3.2	4

The film transfer rates (Figs. 125, 126) are 390 for the kerosene and 127 for the crude oil. The fouling factors will be about as follows:

Shell (crude) factor of	3.0 (Fig. 128)
Tubes (kerosene) factor of	2.0
Total fouling factor	5.0

$$\text{Over-all transfer rate} = H = \frac{1}{1/127 + 1/390 + 0.005} \qquad 66$$

Without periodic cleaning, the rate might be

$$H = \frac{1}{1/127 + 1/390 + 0.009} = 52$$

At a duty of 550,000 B.t.u. per hr., the surface is

log mean temperature difference = 63° (Fig. 65)
The mean temp. difference requires no correction.

$$\text{Surface} = \frac{550{,}000}{66 \times 63} = 132 \text{ sq. ft., with 10 per cent factor} = 145 \text{ sq. ft.}$$

Example 63. Transfer Rate in a Steam Heater.—A tank of fuel oil, 13 A.P.I., 60 viscosity at 210°F., is to be heated from 60 to 110°F. by means of a steam coil. The oil has a pour-point below 60°F. The oil stands in the tank and circulates only by natural-convection. Exhaust steam is used, and it leaves the coil at atmospheric pressure but not cooled below 212°F.

The problem is complicated by the fact that the velocity of the oil must be estimated and because the operation is not continuous. The oil is at 60° at the beginning and ends, after a length of time that depends upon the amount of surface used, at 110°F.

Average temperature of oil is approximately

$$\frac{60 + 110}{2} = 85°\text{F.}$$

Approximate film temperature,

$$\frac{0.95 \times (212 - 85)}{2} + 85 = 148°\text{F.}$$

Viscosity of fuel oil at 148°F. (Fig. 48) = 25 centipoises

Velocity at heating surface (estimate) is probably less than 0.3 ft. per sec. (Table 55). Film transfer rate (Fig. 126) is about 20.

The oil is relatively clean, or it could not be used as a fuel oil, and hence the approximate fouling factors are

Steam	1.5
Fuel oil	7.0
Total	8.5

$$H = \frac{1}{\frac{1}{2{,}500} + \frac{1}{20} + 0.0085} = 17$$

If the heater is to heat the oil in 1 hr. and the duty is 200,000 B.t.u., the surface is

Larger difference = 212 − 60 = 152
Smaller difference = 212 − 110 = 102
log mean temperature difference = 125

$$A = \frac{200{,}000}{17 \times 125} = 94 \text{ sq. ft.}$$

With a 40 per cent factor to allow more rapid heating, the surface is 132 sq. ft

FRICTION LOSSES IN EXCHANGERS

The friction loss through an exchanger is often the governing factor in exchanger design. However, because of the large number of possible arrangements, particularly on the shell-side, the formulation of exact equations is difficult. The loss in pressure on the inside of the tubes can be computed with fair accuracy by the general formulations given in Chap. X, but the losses caused by enlargements, contractions, and turns must be included in the calculations.

Short and Stack[8] have studied the pressure losses on the shell-side of a small commercial exchanger. Half-moon-type baffles were used. They found that the friction factors could be correlated by Reynolds' criterion (Fig. 53) but that the curve was a little lower than that given for copper pipe. However, it is necessary to use a special average velocity and an equivalent diameter. They suggest that u_x, the average velocity, be computed as follows:

$$(u_x)^2 = \frac{(N-1)Au_1^2}{B} + u_2^2$$

where N = number of baffles.
A = distance between baffles.
B = horizontal length of flow.
u_1 = velocity perpendicular to tubes, ft. per sec.
u_2 = velocity parallel to tubes, ft. per sec.

The equivalent diameter D' can be computed by the following empirical formula:

$$D' = \frac{d_t D_s}{N}$$

where d_t = O.D. of tubes, in.
D_s = I.D. of shell, in.

By the use of these equations and approximate friction factors from Fig. 53, the friction loss can be computed as follows:

$$\Delta p = \frac{f \rho L u_x^2}{24 g D'} \tag{78}$$

where Δp = lb. per sq. in.
f = friction factor (Fig. 53).
ρ = density of liquid, lb. per cu. ft.
L = length of passage measured along tubes, in.
g = gravity constant, ft. per sec.^{2}

This equation applies to only the one arrangement of baffles, etc., as used in the experiments, but doubtless it can be used with fair accuracy for other arrangements. The foregoing formula does not account for leakage of oil through the tube holes in the baffle.

A similar equation is presented by Seider and Scott, Jr.,[17] but it applies only to tube bundles that have no baffles.

The friction losses for liquids flowing on the outside of tubes through a single unit of exchanger may be estimated from the following:

Liquids	Lb. per Sq. In. per Ft. of Direct Travel
Light oils: gasoline, kerosene, and hot gas oil	0.04–0.8
Crude oil, gas oil, light lubes, and hot lubes	0.1 –1.1
Viscous stocks	0.3 –1.6

The range is caused by the different velocities that are used. The low values are for 1 ft. per second, and the high for 8 ft. per second.

The pressure-drop through a vapor condenser is often the governing factor in design and especially so for condensers for vacuum systems. The Ross Heater and Manufacturing Company suggests the following formula:[18]

$$\Delta p = \frac{Lu^2}{ks}$$

where Δp = pressure-drop, lb. per sq. in.
L = length of vapor travel, ft.
u = average velocity, ft. per sec.
s = specific volume, cu. ft. per lb.

The constant k probably has a value of 9,000 to 13,000 depending upon the particular design.

TUBULAR VAPOR COOLERS AND CONDENSERS

Tubular equipment is frequently used to cool superheated vapors and to condense them by exchange with the charging-stock. On one side of the exchanger, usually the tube-side, the rates of heat transfer found in the preceding discussion are valid. On the other, or shell-side, of the exchanger, a new set of conditions arise. Vapor cooling is a straightforward problem, but the condensation of complex vapor mixtures in the presence of steam is indeed a complicated problem.

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[17] McAdams, W. H., "Heat Transmission," p. 119, McGraw-Hill Book Company, Inc., 1933.

[18] Heat Exchangers, *Bull.* 350, 1931.

Structural Design.—Fundamentally the structural design of condensers differs little from the design of simple liquid-to-liquid heat exchangers. However, ample space must be provided on the outside of the tubes so that prohibitive vapor velocities and friction losses will not occur. This problem becomes of prime importance in the design of vacuum condensers. In such designs, the friction loss must not exceed a few millimeters, and often the condenser is designed primarily with regard to friction losses. Oil vapors are the highest temperature materials commonly handled in the refinery. In order to avoid unequal expansions, condensers are usually built in several units so that the temperature difference across each unit of exchanger is not large. A temperature difference of 75°F. is considered safe. If the vapor is at a very high temperature, the cooling stock must be heated by other exchangers before it is passed through the vapor condensers. In other words, a large temperature differential between the two stocks cannot be permitted. The vapor is usually admitted to the top of the condenser so that the condensate, which might entrain, is carried toward the liquid line. At the same time the condensate drips or flows over the remaining tubes. Transfer rates for such equipment are given on page 402.

Most manufacturers have developed so-called drip-type condensers embodying the foregoing principles. The advantages claimed for the drip-type condenser are

1. Low-pressure-drops.
2. Less entrainment.
3. The condensate leaves at the same temperature as the remaining uncondensed vapor, and hence little or no reheating or revaporization of the light ends occurs.
4. Ideal countercurrent flow is more nearly approached.

Erosion by droplets of liquid and by high vapor velocities requires thicker tubes than those used in exchangers.

Film Conditions during Condensation.—The film conditions are different in all parts of a condenser. For convenience the following zones may be adopted:

1. Cooling oil vapor, steam, or both.
2. Condensing vapor, cooling vapor, and cooling the condensate.
3. Condensing steam and cooling oil.
4. Cooling oil and water.

These zones all tend to overlap. As an example, condensation starts soon after cooling of the superheated vapors begins; the cooling of vapor, steam, and condensate occurs throughout the condensation of the vapors; and, finally, the last vapor is not condensed until the steam is condensed. However, for design purposes it is necessary to adopt these zones and assign transfer rates to each of them if dependable rates are to be attained. It is apparent that each of the zones has a different mean temperature difference and that under certain conditions the temperature of the cooling medium may tend to be even higher than the temperature of the heating medium on the other side of the tube.

The total heat to be removed is usually computed as heat required (1) to cool vapor and steam, (2) to condense the vapor, (3) to condense steam, and (4) to cool oil and water. These items need not be computed at the actual conditions existing in the condenser because, as mentioned in the chapter on heat and material balances, the total quantity of heat that is removed between the fixed inlet and outlet conditions is a constant, regardless of the intermediate conditions.

However, when the mean temperature difference is computed, the actual temperatures throughout the equipment must be used. In the condensation zone, the temperature may be computed with accuracy by means of the equilibrium condensation curve of the oil vapor, corrected for the total pressure within the condenser and for the partial-pressure effect of the steam. Such a method need not be tedious because the designer soon becomes facile at drawing condensation curves and can often accurately estimate the condensation range without computations. For example, steam condenses in an atmospheric light oil condenser between 205 and 185°F. unless an abnormally large quantity of steam is used. In special problems, such as the design of vacuum condensers or condensers handling large quantities of steam, the labor in drawing the curves, etc., is justified because more simple methods are not dependable.

The vapor usually condenses almost entirely between the inlet temperature and the steam-condensation temperature; but if the vapor is superheated, an additional simple cooling zone must be recognized. Even in the cooling zone a small quantity of vapor is condensed because of the wide boiling-range of all petroleum products. In the so-called vapor-condensation zone a cooling of both vapor and liquid-condensate takes place as well as condensation, and hence most experimenters have found it necessary to use a combined condensing, vapor-cooling, and condensate-cooling coefficient for the vapor-condensation range. The coefficients given in this chapter are combination coefficients of this kind. The steam-condensation temperature is usually not a constant, and its condensation range may be computed by correcting the condensation temperature, at the total pressure, for the partial-pressure effect of the remaining vapors. In the special case in which a very high-boiling vapor is condensed with steam, two distinct zones of condensation may appear and the steam will condense at nearly a constant temperature. Except in special cases the steam may be assumed to condense at a constant temperature of about 195°F. The pressure-drop in ordinary condensers may be neglected in drawing the condensing curves, but in vacuum condensers the pressure-drop becomes of great importance. The following examples will prove valuable in clarifying the computation methods:

Example 64. Transfer Rate for a Pressure Distillate Condenser.—A pressure distillate condenser is to be designed for the following materials:

	Lb. per Hr.
P. D. and reflux (57 A.P.I.)	63,000
Cracked gas (wet)	2,000
Steam	6,000

The materials are available at 305°F., and the vapor is not superheated. Water is available at 72°, and it will be heated to 120°F. Pressure at the top of the tower = 10 lb. per sq. in.

Duty of Condenser.

Basis: 1 hr.

Assume cooling to 180°F. condenses all vapor and steam. Assume steam condenses at 195°F. These assumptions can be approximately computed by the methods used in Example 65.

Zone 1: Cooling vapor and steam. No such zone.
Zone 2: Condense vapor between 305 and 195.
Cool steam and vapor to 195.
Cool condensate to 195.

		B.t.u. per Hr.
Cool vapor or condensate	$63{,}000(305 - 195)\dfrac{0.60 + 0.46^*}{2} =$	3,670,000
Cool gas (Fig. 34)	$2{,}000(305 - 195) \times 0.52 =$	114,000
Cool steam	$6{,}000(305 - 195) \times 0.5 =$	330,000
Condense vapor (Fig. 37)	$63{,}000 \times 131 =$	8,229,000
		12,343,000

* Average liquid and vapor specific heat.

Zone 3: Condense steam at 195.

Latent heat of steam = 981

6,000 × 981 = 5,890,000 B.t.u. per hr.

Zone 4: Cool oil, water, and gas.

	B.t.u. per Hr.
63,000(195 − 180) × 0.565	= 532,000
6,000(195 − 180) × 1.0	= 90,000
2,000(195 − 180) × 0.5	= 15,000
	637,000

The percentage of heat that is absorbed in each zone and the rise in water temperature in each zone, for countercurrent flow, are:

Zone	B.t.u.	Per cent	Rise in water temperature (total 48°)
1			
2	12,343,000	65.4	31
3	5,890,000	31.2	15
4	637,000	3.4	2
Total	18,870,000	100.0	48

The temperatures in the zones are shown in Fig. 129.

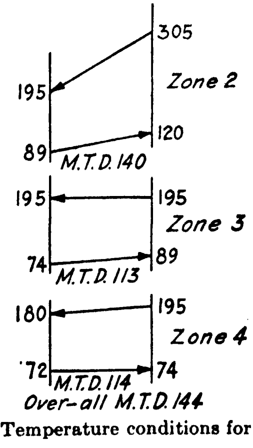


FIG. 129.—Temperature conditions for Example 64.

Computation of Transfer Rate.—Assume a water velocity of 2 ft. per sec. in the tubes. This corresponds to a water film rate of 350.

The surface required for each zone can be computed separately and added together, thus:

Zone	Duty	Mean temp. diff.	h_o	h_w	R_f*	H	A	Notes
1. Cooling vapor.....	....	...	...	...	.....	..	.....	No such zone
2. Condensing vapor.	12,343,000	143	150	350	0.006	64	1,350	Table 56
3. Condensing steam.	5,890,000	113	400	350	0.007	81	643	Page 405
4. Cooling liquid.....	637,000	114	45	350	0.009	29	192	Page 405
Total.............	18,870,000	...	...	...	.....	..	2,185	

* See Fig. 128. A water factor of 5, and different factors for each of the other conditions.

As a comparison, the over-all transfer rate that corresponds to the four zones is

$$H = \frac{18{,}870{,}000}{2{,}185 \times 144} = 60.0$$

In vacuum condensers the foregoing method (Example 64) becomes more involved. Approximations of the steam-condensing temperature, etc., cannot be relied upon. In most modern vacuum plants a large quantity of steam is used to reduce the vaporization temperature of the oil. This steam passes through the partial condensers and is finally condensed in a barometric condenser. Thus the pressure in the barometric condenser and in the partial condenser is dependent upon the vapor-pressure exerted by the cooling water. With cold water and several steam jets, the barometric condenser can be operated at 8 mm. pressure, and hence the partial condenser operates at pressures of 10 or 12 mm. or above, depending upon the processing plan. Sometimes these partial condensers are built in several units so that different products, such as gas oil and wax distillate, may be collected from the different units. A poor separation is permissible in this case because wax distillate can be more easily filter-pressed if it contains some gas oil.

If the condensation is conducted in several units or steps, with the condensate removed separately from each partial condenser, each unit may be handled as a separate condenser. For example, if wax distillate and gas oil are separated in a partial condenser, the vapors of wax distillate and gas oil are cooled in the first unit and condensation occurs along the equilibrium condensation curve of these mixed vapors. The wax distillate is withdrawn from this unit, and the remaining gas oil vapor is condensed according to the equilibrium condensation curve of the gas oil vapor alone (Figs. 130 and 131).

The condensing coefficients are lowered greatly by vacuum. The exact values are not known, but it is customary practice to decrease the atmospheric condensation coefficients by half.

Example 65. Design of Vacuum Surface Condenser.—A large vacuum condenser is to handle the following materials per hour:

106,000 lb. of wax distillate and reflux, 31 A.P.I.
12,000 lb. of gas oil, 33 A.P.I.
1,400 lb. of steam

The wax distillate and gas oil are to be separated by partial condensation in four units of condenser. Three of these are for wax distillate, and one for gas oil. The first of the three wax distillate condensers supplies hot reflux to the tower, but cold reflux is also used.

The following pressures are assumed for purposes of calculation. In an actual design the accuracy of the assumed pressures should be checked after the tentative design is completed.

	Mm. of Mercury
Pressure at barometric	21
Loss in vapor line	2
Loss in Unit 4	1
Loss in Unit 3	1
Loss in Unit 2	2
Loss in Unit 1	3
Pressure at top of tower	30
Temperature at top of tower	490°F.

The approximate condensation and true-boiling-point distillation curves of the products are shown in Fig. 130, and a diagram of the system is shown in Fig. 131.

Condensation Curves under Vacuum. *Partial Condenser* 1 (*Hot Reflux Condenser*).—The conditions are such that equilibrium condensation (page 226) occurs in all four of the condensers. The condensation curves are computed by means of Fig. 76.

70 per cent point of T.B.P. curve	765°F.
10 per cent point of T.B.P. curve	620°F.
Slope of T.B.P. curve	$^{145}/_{60} = 2.42°$ per per cent
Corresponding slope of flash curve	0.8 (Fig. 76)
50 per cent point on T.B.P. curve	718°F.
Corresponding 50 per cent point on flash curve	684°F.

100 per cent point on flash curve $= 684 + 0.8(100 - 50) = 724$°F.

The curve is drawn through the 50 and 100 per cent points.

The data given in curves 1 and 2 (Fig. 130) apply to condensation at atmospheric pressure, and hence curve 5 for vacuum conditions must be computed.

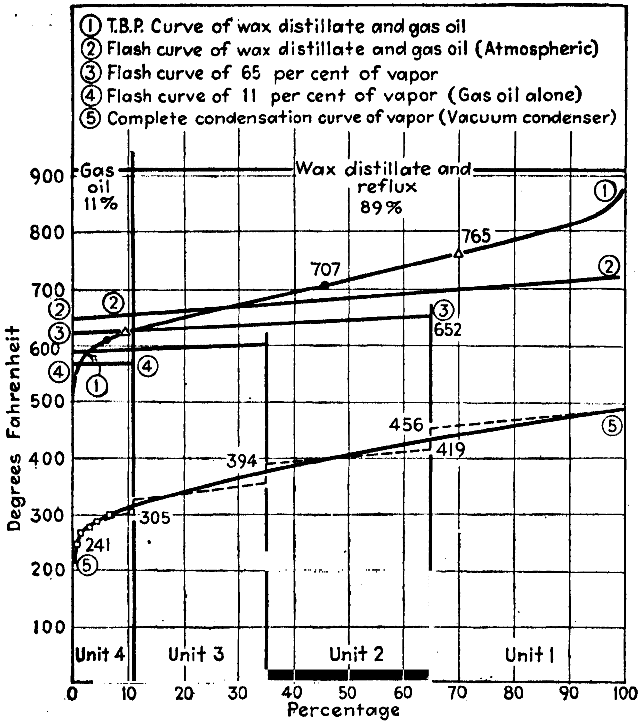


FIG. 130.—Condensation temperatures in vacuum condenser. Refer to Example 65.

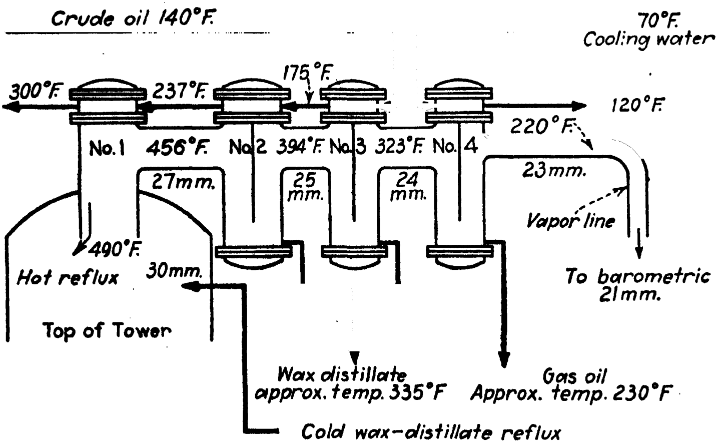


FIG. 131.—Condenser arrangement for Example 65. (See also Fig. 130.)

The total pressure at the inlet to Condenser 1 is 30 mm., but at the end it is (30 − 3), or 27 mm. Furthermore, steam is present, and it further reduces the partial-pressure of the oil vapor and decreases the temperature of condensation.

$$\begin{array}{lcccr}
\text{Mols W.D.} & = & \dfrac{106{,}000}{320} & = & 331.0 \\
\text{Mols gas oil} & = & \dfrac{12{,}000}{242} & = & 49.6 \\
\text{Mols vapor} & & & = & \overline{381.0} \\
\text{Mols steam} & = & \dfrac{1{,}400}{18} & = & 78.0 \\
\text{Total mols} & = & & & \overline{459.0}
\end{array}$$

$$\text{Partial-pressure} = 30 \times {}^{381}\!/_{459} = 24.9 \text{ mm.}$$

The atmospheric initial-condensation temperature (724°F.) corrected to 24.9 mm. (Fig. 52) gives a temperature of 492°F.

Temperature at the Outlet of Unit 1.

About 122 mols of hot reflux are condensed in Unit 1 so that at the outlet the partial-pressure is

$$27 \times \frac{381 - 122}{459 - 122} = 20.8 \text{ mm.}$$

Correcting 696°F. to 20.8 mm. gives an outlet temperature of 456°F. These temperatures are shown on Figs. 130 and 131.

Partial Condenser Unit 2.—The atmospheric condensation curve for the remaining 65 per cent vapor is computed in a manner similar to the method used for Unit 1. This curve is shown as 3 (Fig. 130). As the condensate is removed from Unit 1, the vapor must be cooled in Unit 2 before condensation starts. Note curve 5 (Fig. 130) and particularly the two points at 65 per cent. In practice, no sharp break in the temperature is noted because pure countercurrent flow is not attained and perfect equilibrium condensation does not occur.

Furthermore, it would appear in Fig. 130 that the hot reflux boils between exactly 753 and 890°F. Actually, the wax distillate and the hot reflux have different boiling-ranges but much the same composition because of the very poor separation obtained by partial condensation.

70 per cent B.P. of 65 per cent of remaining vapor	707°F.
10 per cent B.P. of 65 per cent of remaining vapor	607°F.
Slope of distillation curve	1.67
Slope of vaporization curve	0.35
50 per cent on distillation curve	677°F.
50 per cent on vaporization curve	635°F.
100 per cent point on vaporization curve	652°F.

Note curve 3 (Fig. 130).

Partial-pressure at inlet to Unit 2 is the same as for the outlet of Unit 1, or 20.8 mm. Correcting 652 to 20.8 mm. gives 419°F.

About 130 mols are condensed in Unit 2 so that the partial-pressure at the outlet of 2 is

$$25 \times {}^{129}/_{207} = 15.5 \text{ mm.}$$

Correcting 635° to 15.5 mm. gives 394°F. Partial condenser Unit 3 was computed in a similar manner.

Partial Condenser Unit 4.—By the time Unit 4 is reached, the amount of noncondensible gases (steam) has become relatively so large that a more detailed analysis is necessary. The following tabulation was computed (curve 4, Fig. 130) by using the same general principles that were used in studying Units 1 and 2.

The pressure-drop is very small (1 mm.), and hence a constant pressure of 23.5 mm. was used throughout the entire unit. Likewise the flash curve 4 is so flat that a temperature of 563° was used to represent the entire curve.

Per cent vapor remaining	Mols not condensed (approx.)	Partial-pressure	Condensation points
11.0	50	8.6	305
7.5	33	6.5	296
5.0	22	4.8	283
3.5	16	3.8	274
1.5	11	2.7	264
1.0	6	1.4	241

The sharply curving tail on the front of the condensation curve shows that all of the vapor can never be completely condensed until the steam is condensed. Refiners find that the water leg of the barometric condenser always contains oil and wax-stocks, and traps or skimming devices must be installed.

Thermal Duties of the Units. *Unit* 1 (47,000 *Lb. Condensed*).—Condensing zone throughout

		B.t.u. per Hr.
Cool vapor	$71{,}000(490 - 456) \times 0.56$	= 1,350,000
Cool steam	$1{,}400(490 - 456) \times 0.5$	= 238,000
Cool	$47{,}000(490 - 456)\left(\frac{0.68 + 0.55}{2}\right)$	= 983,000
Condense, approx.	$47{,}000 \times 92$ (Fig. 38)	= 4,320,000
		6,891,000

For the other units the duties are about as follows:

Condenser unit	Lb. condensed	Temperature range	Approx. duties, B.t.u. per hr.
1	47,000	490–456	6,891,000
2	39,000	456–394	7,213,000
3	20,000	394–323	4,058,000
4	12,000	323–220	2,856,000
Total................	......	....	21,018,000

Transfer Rates, Surfaces, and Temperature Differences.—Crude oil is heated from 140 to 300°F. in the first three units, and water is heated from 70 to 120°F. in the fourth unit. The crude oil velocity is 3 ft. per sec., and the water 2 ft. per sec. The temperature ranges are shown in Fig. 132. One-inch tubes are used throughout.

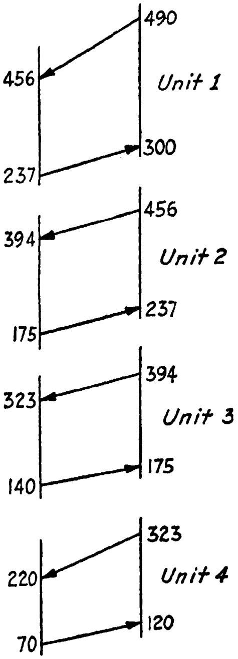


FIG. 132.—Temperatures for Example 65.

The transfer rates are considered as two items, one pure condensing and the other cooling of vapors. Table 60 shows the completed calculations.

Note that the logarithmic mean temperature difference gives confusing results if it is used for the three units together. Its use in this manner shows an over-all rate of heat transfer (11.4) that is lower than the transfer rates in any of the three units.

TABLE 60.—COMPUTATIONS FOR SURFACES IN EXAMPLE 65

Unit No.	Duty	Mean temp. diff. (logarithmic)	Mass velocity† (approx.)	h_o	h_{tubes}	R_f	H	A
1. Condensing	5,303,000	204	. . .	23‡	160	0.013	15.9	1,640
Vapor cooling*	1,588,000	204	1.0	11	160	0.013	9.0	865
Over-all	6,891,000	204	. . .	. . .	. . .	. . . . .	13.6	2,505
2. Condensing	5,730,000	219	. . .	25‡	130	0.013	16.5	1,580
Vapor cooling*	1,483,000	219	0.8	10	130	0.013	9.0	752
Over-all	7,213,000	219	. . .	. . .	. . .	. . . . .	14.1	2,332
3. Condensing	3,136,000	196	. . .	27‡	85	0.012	16.2	990
Vapor cooling*	922,000	196	0.5	7	85	0.012	6.1	770
Over-all	4,058,000	196	. . .	. . .	. . .	. . . . .	11.8	1,760
1, 2, and 3, over-all	18,162,000	243	. . .	. . .	. . .	. . . . .	11.4	6,597
4. Condensing	2,135,000	187	. . .	28‡	400	0.011	20.2	565
Vapor cooling*	721,000	187	0.2	3	400	0.011	2.9	1,330
Over-all	2,856,000	187	. . .	. . .	. . .	. . . . .	8.0	1,895

* Some liquid cooling also included.

† Dependent on velocity on shell-side.

‡ Condensing coefficients are halved for vacuum service.

COIL-IN-BOX CONDENSERS AND COOLERS

In the past these equipments have been standard, and even today they are used extensively for final cooling before storage. Heat transfer rates are low in this type of equipment owing (1) to the low velocities that must be used and the low natural-convection rate and (2) to the gradual accumulation of pipe scale and fouled surfaces on the water side. Special cast-iron condenser sections with ribbed outside surfaces, such as the Stirling section of the American Radiator Company, are sometimes used. The main advantage of this condenser section is the large vapor space afforded and the compact arrangement that is possible. To allow for the rapid decrease in vapor volume, coil-in-box condenser coils are usually built as a series of large-diameter pipes

CHAPTER XXII

TUBESTILL HEATERS

When pipestills or tubestills were first built, the important part that radiation plays in any furnace type of heater was not appreciated and the first stills were nearly pure convection types of stills (Fig. 133*f*). In such stills the tubes nearest to the flame absorb heat at a very high rate, and the tubes nearest the stack absorb very little heat. Such an arrangement was unsatisfactory because coke was deposited in the tubes that were heated by radiation and the final tubes absorbed so little heat that the efficiency was low. By costly experience it was found that when the offending radiant tubes (hot ones) were removed, the other tubes began to overheat and the removal of tubes in the radiant section only aggravated the condition. When designers finally realized that a large proportion of the pipestill surface should be in the radiant section, the pipestill was developed into the useful type of heating equipment that it now is.

Advantages of the pipestill over shellstill equipment are as follows:

1. They are unquestionably best suited for continuous operation. From the standpoint of operation, a continuous process is usually the most economical because the operating conditions such as temperature, pressure, and rate of flow can be easily controlled and studied. Continuous operation was also an important factor in the development of such obviously useful operations and equipment as flash vaporization, heat-exchange, multiple-draw fractionating towers, and exact control instruments. Without continuous heating, these operations could never have been developed into the position of importance that they now occupy.

2. The pipestill adapts itself to any sort of a heating operation because the rate of heating can be easily controlled. The rate of heat input can be controlled by adjusting the relative proportion of radiant and convection surface, by the use of a recirculating quantity of flue gas, by preheating the air, by changing the fuel

or character of the flame, and last, by varying the velocity within the tubes.

3. The average rate of heat transfer can be increased without overheating the oil stock. This permits the thermal efficiency of the pipestill to be relatively high. Thus far, economic conditions have limited the economic thermal efficiency to about 75 per cent, but many stills have been built that operate at an efficiency of 85 per cent.

In a shellstill, local overheating occurs near the bottom of the still. Oil is decomposed, which causes a loss of yield, and the bottom plates are frequently weakened so that they must be replaced.

4. Pipestill operation is flexible. A still designed to operate at 75 per cent efficiency can, at a low capacity, operate at 80 per cent efficiency and at a high capacity at about 70 per cent efficiency. The capacity can often range between 50 and 200 per cent of the rated capacity without causing serious deleterious effects. During the development of pipestills, the redistillation operations necessary for such stocks as pressure distillate, kerosene, special naphthas, brightstock solution, pressed distillate, and "slops" were conducted in shellstills. Perhaps this was due, at least in part, to the existence of shellstills in the plant. At any rate, refiners are now installing pipestill units for any or all of these rerunning operations. In some small plants the raw stocks are allowed to accumulate for several weeks and then are redistilled in a pipestill unit in a few days of operation. Thus a single pipestill unit may be used to process several stocks.

5. Pipestill heaters greatly reduce the danger of fire. Although fires are perhaps more frequent with pipestills than with shellstills, the fires are not of such a dangerous nature. In normal-size pipestills the quantity of oil that is present in the still at any time amounts to only about 60 bbl., and most of this may be discharged into a sump and extinguished with steam. At the same time the furnace interior and header boxes can be filled with steam so that little oil burns. Several hundred barrels of oil may be present in a shellstill when a fire occurs, and the possibility of an explosion or the escape of flaming oil into the refinery yard and drains is indeed serious.

6. The compact nature of a pipestill distillation equipment should not be overlooked. A pipestill unit for processing

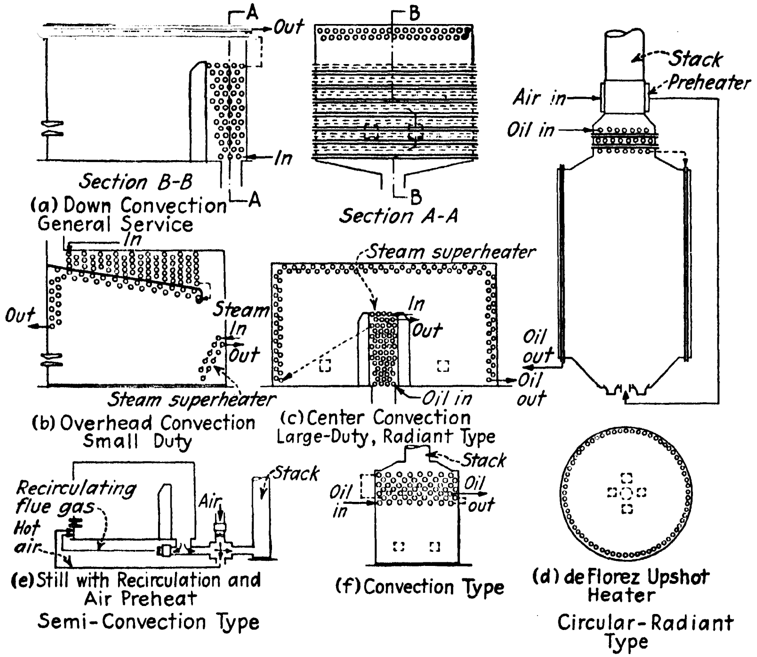
10,000 bbl. per day can be installed within a 50 by 50 yd. area. Such a unit will replace a battery of at least 12 shellstills. However, the saving in space and personnel is not the main advantage of a compact unit. The operation can be more easily supervised, the stillman will give more attention to details if distances are not great and records can be taken with ease. The entire operating data may be recorded in a single control room, and the responsibility for operation may thus be placed on one man.

Indirectly, the pipestill is largely responsible for the development of modern vacuum distillation plants. The modern vacuum processes could not have been developed without the combined advantages of controlled heating and flash vaporization.

Types of Stills.—All modern pipestills are built with two distinct heating sections: a radiant section and a convection section. Figure 133 indicates diagrammatically the flow in several types of heaters.

The type shown in Fig. 133*a* has been for many years the standard design. The still is usually less expensive than the other types, but it is being displaced by the other types because the radiant roof tubes above the partition wall tend to become overheated. Furthermore, a large percentage of radiant-absorption surface cannot be provided unless the still is very wide, and such a design proves to be expensive. In this type usually about 40 per cent of the heat is absorbed in the radiant section and 30 per cent in the convection section. Figure 133*b* shows a type that is particularly adapted to processing small amounts of oil. The radiant and convection sections are separated by metal partition plates, with insulating material between them. This partition rests on the tubes, thereby eliminating an expensive suspended refractory arch. The distribution of radiation is poor, but this causes no difficulty in the heating of normal stocks.

The center-convection-type radiant heater shown in Fig. 133*c* provides a large percentage of radiant surface and is adapted to the processing of large quantities. The distribution of radiation in the furnace box is excellent but not so good as in the cylindrical heater shown in Fig. 133*d*. In the center-convection still, enough radiant surface can be provided, without undue expense, to absorb 65 per cent of the total heat liberation as radiant heat. The radiant-absorption rate in this type of still can be reduced by using a large amount of radiant surface until it compares with the rates that are obtained in flue-gas recirculation furnaces. The heater shown in Fig. 133*d*, from a theoretical standpoint, is an ideal heater, but it is expensive. A tall superstructure is necessary for the removal of tubes. At the same time the vertical position of the still makes it act partly as a stack, and hence only a short stack is necessary. This type is particularly suited for vapor-phase cracking, although it is equally successful in ordinary processing. In the case of vapor-phase cracking the



(a) Down Convection General Service

(b) Overhead Convection Small Duty

(c) Center Convection Large-Duty, Radiant Type

(e) Still with Recirculation and Air Preheat Semi-Convection Type

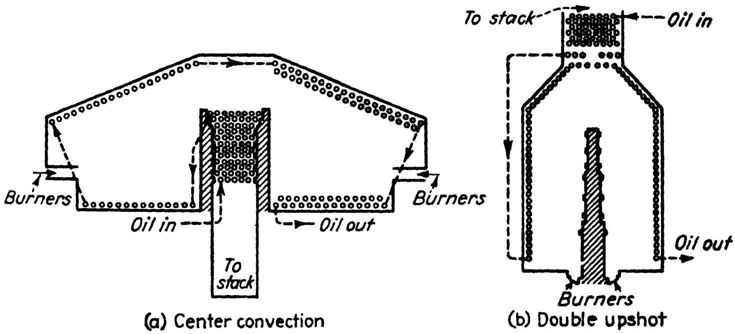
(f) Convection Type

(d) deFlorez Upshot Heater Circular-Radiant Type

FIG. 133.—General types of pipestill construction.

cost of such a still is justified because, to the author's knowledge, no petroleum oil heating problem is more delicate than the heating of petroleum vapor at decomposition temperatures. In this type, as high as 70 per cent of the heat liberation may be absorbed in the radiant section.

Modern developments have been directed at two improvements: (1) symmetrical arrangements by which flue-gas turbulence and sharp changes in the direction of the flue gas are avoided and (2) partition arrangements by which the heat input into various parts of the still can be regulated independently. These improvements are embodied in the types of stills indicated in Fig. 134. Regulation of heat distribution is possible by the use of several small burners on each side of the central bridge walls and by the degree of exposure of the flame from the firing-tunnels of the burners. By avoiding turbulence and currents of hot gas, hot spots or flame impingement are brought to a minimum, and unusually high radiant-absorption rates can be attained without tube failure. The upshot-type stills (similar to "Equiflux") are most symmetrical and can attain very high rates, but the center convection type is perhaps best for heating two separate coils or in adjusting the rate of heating in a constant temperature soaking zone. Radiant-absorption rates of 45,000 B.t.u. per square foot of projected area have been obtained commercially in some of these stills.



(a) Center convection (b) Double upshot

FIG. 134.—Modern tube arrangements for pipestills.

The principles of flue-gas recirculation and air preheating as indicated in Fig. 133e may be applied, with modifications, to any of the foregoing types. A portion of the flue gas is circulated back into the radiant section by a fan. Here the flue gas is reheated by the flame causing a lower flame temperature and a milder radiation rate, and at the same time the high gas velocity increases the rate in the convection section. The greater the ratio of recirculating flue gas to the flue gas entering the stack the more the heat-duty is transferred from the radiant to the convection section. Recirculation allows a precise regulation of the absorption rate, and until the development of radiant-type stills the recirculating type was used for nearly all cracking processes or delicate heating operations because of the low radiant rates.

Preheating the air that is used in combustion has just the reverse effect. It tends to increase the absorption rate in the radiant section and to increase the flame temperature. To be most effective, the air should be heated by only the gases that are passing to the stack. To store too much heat in the air, as by cooling the entire recirculating stream of gases, would defeat the purpose of flue-gas recirculation. Nevertheless, air preheat provides a means of cooling the stack gases and thereby increases the efficiency of the still.

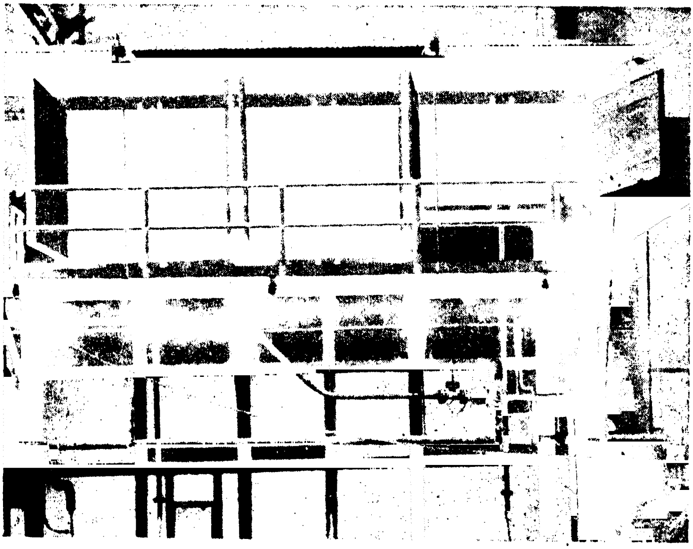


FIG 135.—Overhead-convection still (header-boxes open). (*A. J. Smith Engineering Company.*)

The efficiency of a process can be increased in two main ways. The loss through the walls and in the stack gas from the furnace can be decreased, or heat can be saved from the products of the process. The use of air-cooled walls, aside from the preservation of brickwork, has often been referred to as an economy. Unless the loss through the walls is decreased, no economy is effected.

The heat that is absorbed by heat exchangers is often credited as a direct saving in heat. Such is not always the case because the efficiency of the still decreases as the temperature of the charge-stock is increased by exchangers. As an example, consider a pipestill distillation unit that operates with no exchangrs and at a stack gas temperature of 350°F. The stack loss is only about 8.4 per cent (Fig. 56). If the charge-stock is then heated by exchangers to 300°F., the stack temperature will be about 550°F. and the stack loss 14 per cent. In such a case the saving of heat by raising the temperature of the charge-stock from 100 to 300° must more than compensate for the decrease in the efficiency of the still. The exchangers do save heat, but they cannot be accredited with saving the amount of heat that is represented by the rise in temperature from 100 to 300°. A study of the economics of the complete unit, including both the pipestill and the exchangers, is the only way to determine the amount of heat that is actually saved.

RADIATION

The problem of evaluating the percentage of radiant absorption that will occur in a particular pipestill, and the distribution of this radiation throughout the furnace cavity, has always been difficult. However, in recent years, owing primarily to the efforts of Professor Wohlenberg[1,2,3] of Yale and Professor Hottel[4,5,6,7] of the Massachusetts Institute of Technology, a comprehensive theoretical background has been developed. By this background the existing empirical data can be explained with gratifying success, and theoretical treatments are so sound that plant data can be checked closely if the data are sufficiently extensive. Still more recently work by Wilson, Lobo, and Hottel[8] has placed at our command a correlation of a number of plant experiments on radiation.

[1] Wohlenberg and Morrow, Radiation in the Pulverized Fuel Furnace, *Trans. A.S.M.E.*, **47**, 127 (1925).

[2] Wohlenberg and Lindseth, The Influence of Radiation on Boiler Surface and a Simplified Method for Its Calculation, *Trans. A.S.M.E.*, **48**, 849 (1926).

[3] Wohlenberg, W. J., *Mech. Eng.*, **52**, 853 and 915 (1930).

[4] Hottel, H. C., Heat Transfer by Radiation from Non-luminous Flames, *Ind. Eng. Chem.*, **19**, 888 (1927).

[5] Hottel, H. C., Radiant Heat Transmission, *Mech. Eng.*, **52**, 699 (1930).

[6] Haslam and Hottel, Combustion and Heat Transfer, *Trans. A.S.M.E.*, **50**, *Fuel Steam Power Division*, p. 9 (1928).

[7] Hottel, H. C., Radiant Heat Transmission between Surfaces Separated by Non-absorbing Media, *Trans. A.S.M.E.*, *Fuel Steam Power Division*, **53**, 265 (1931).

[8] Heat Transmission in Radiant Sections of Tube Stills, *Ind. Eng. Chem.*, **24**, 486 (1932).

Physical Nature of Radiation.—Radiation may be considered as an outlet for the chemical energy that is set free during combustion reactions. The heat energy that is liberated during combustion is confined in such a small space at the start of combustion that either a very high temperature is attained or heat must be dissipated to the surroundings by radiation, convection, or conduction. No doubt heat is initially used in heating the reactant materials to the flame temperature by conduction. However, if all of the heat were utilized in this manner, the theoretical flame temperature would be attained, and experience teaches that this temperature is never reached in ordinary combustion reactions.

The two gaseous materials that are most active in producing radiation are carbon dioxide and water vapor. Most of the radiation from nonluminous flames has wave lengths corresponding to the wave lengths that are emitted by these two molecules. Radiation from luminous flames differs from nonluminous because finely dispersed carbon or solid particles are present in the flame. These particles absorb heat by conduction and convection and are even more effective than gaseous molecules in radiating energy. The difference in the actual flame temperature and the theoretical flame temperature is a direct comparison of the radiant properties of a fuel.

Radiant-absorption Rate.—Radiation between solid surfaces is dependent upon the fourth power of the temperature difference and upon a constant, the value of which is dependent on the kind of material and the condition of the surface. Radiation from a flame, as in pipestill or boiler furnaces, is governed by the same laws except that the size of the flame and the conditions within the flame are so difficult to evaluate that empirical relationships have been adopted. The most important factors that affect radiation from flames are (1) percentage of total heat that is absorbed as radiant heat, (2) ratio of air to fuel, (3) arrangement and spacing of absorbing surface, and (4) kind of fuel.

Regarding the first of these, let us consider a flame burning within a furnace whose walls consist entirely of absorbing surface. Rays of radiation proceed in all directions from the flame; and with the exception of the small amount of heat that is used in heating the intervening gas, all the heat from the flame is absorbed by the cool surface. In this case, a *large percentage* of the heat is transferred by radiation, although the rate of heat absorption per square foot of surface is low. If all the absorbing surface, except a single tube, is removed from such a furnace, the radiation strikes the refractory walls and is reflected or reradiated about the furnace interior so that the single tube receives a relatively larger amount of radiation per unit of surface. Although the single tube absorbs heat at a high rate, it absorbs a relatively small percentage of the total heat liberation.

The ratio of air to fuel is important mainly because it affects the flame temperature. The larger the quantity of air (or products of combustion) that must be heated in the flame the lower will be the resultant flame temperature. Thus large quantities of excess air reduce the radiant absorption. For the same reason the recirculation of flue gas reduces the flame temperature, but air preheat increases it. Obviously the higher the flame temperature the greater the emission of radiation. The arrangement of the cooling surfaces also affects the rate of radiant absorption. The closer the surface is to the flame the greater the amount of radiation that falls upon it. Thus corners and ends of furnaces receive less radiation than other surfaces.

These factors have been related by Wilson, Lobo, and Hottel[8] by the following equation:

$$R = \frac{1}{1 + \dfrac{G\sqrt{\dfrac{Q}{aA}}}{4{,}200}} \tag{79}$$

where R = fraction of heat liberation (above 60°F.) that is absorbed by the cold surfaces in the combustion chamber.

G = air-fuel ratio, lb. of air per lb. of fuel. For flue-gas recirculation: lb. of air and recirculated gases per lb. of fuel.

Q = total heat developed in the flame (above 60°F.), B.t.u. per hr. This may consist of the net heating value of the fuel, heat in air or in recirculated gases, and sensible heat in the fuel or atomizing steam.

A = area of plane replacing tubes, sq. ft. (projected area).

a = a factor by which A is multiplied to obtain the effective cool surface. Usually 0.98 (Fig. 136).

This equation applies to any conventional box-type furnace with radiant tubes any number of rows deep, with or without air preheat, with or without flue-gas recirculation, and with any percentage of excess air. The factor a may be obtained from Fig. 136,[9] but for normal tube arrangements, such as two rows of tubes spaced at a center to center of about twice the tube diameter, the value of a is 0.98. The relative absorption rates in the first three rows of tubes, when only three are present, is approximately 7:3:1 so that the third row is of little value.

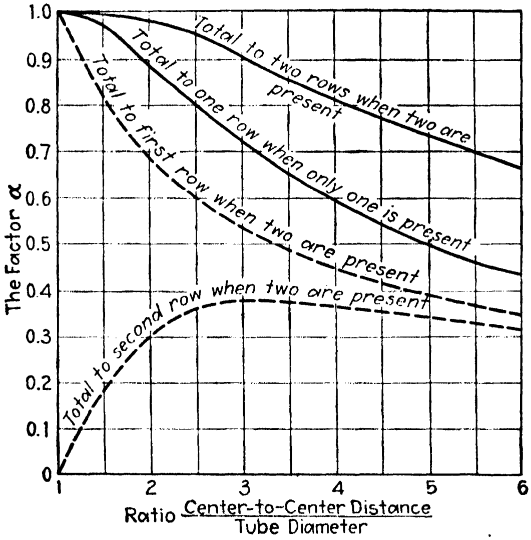


FIG. 136.—Distribution of radiation with regard to arrangement of tubes. (*Hottel, Mechanical Engineering.*)

A study of this equation for the effect of the type of fuel is useful. Table 62 is based on the fuel analyses and data given in Chap. XI. The radiant-absorption factors and rates of absorption per square foot of projected area are computed for 30 per cent excess air when 50,000 B.t.u. are liberated for each square foot of projected tube surface. Thus the common refinery fuels do not give largely different rates of radiation. However, gas flames give a slightly milder rate of heating.

The effect of the percentage of excess air is indicated in Fig. 137. The radiation rates for the two extreme fuels, *i.e.*, dry natural gas and heavy fuel oil, are shown for 0, 25, 50, and 100 per cent excess air. Other fuels can be represented by lines between these two extremes. Table 62 will be useful in judging the approximate position of these lines. This chart may be used directly in the design of simple furnaces, but it should not be used for furnaces using air preheat or flue-gas recirculation. With proper burners and an experienced fireman, it is possible to fire with less than 25 per cent excess air. In the past, many furnaces have been operated with 100 or even 200 per cent excess air because the still was originally designed with too little radiant surface with the result that the absorption rate was too high.

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[9] HOTTEL, H. C., *Mech. Eng.*, **52**, 699 (1930).

TABLE 62.—COMPARISON OF RADIATION PROPERTIES OF REFINERY FUELS

Fuel	Heating value		Lb. flue gas per lb. fuel	Fraction absorbed by radiant section	B.t.u. absorbed per sq. ft. (proj.)
	Gross	Net			
1. Pure methane	1,009	909	23.5	0.443	22,100
2. Dry natural gas	1,160	1,051	23.2	0.445	22,200
3. Wet cracked gas	2,058	1,893	22.0	0.462	23,200
4. Wet natural gas	1,360	1,239	21.0	0.482	24,100
5. 24.4 A.P.I. Ky. topped crude	19,358	18,168	19.7	0.485	24,250
6. 9.2 A.P.I. cracked tar (M.C.)	18,274	17,324	18.8	0.497	24,850
7. 7.6 A.P.I. resid. fuel oil (Calif.)	17,970	17,075	18.4	0.502	25,100
8. Bituminous coal (Mo.)	13,533	13,098	13.6	0.578	28,900*

* Of questionable value because Eq. (79) is not for solid fuels.

If a low rate of absorption is not necessary but gas is available and must be burned, a mixture of oil and gas may be fired together. The luminosity or radiating power of such flames appears to be almost as good as for pure oil flames. Hence for such mixed flames the curves in Fig. 137 for oil flames may be used. The radiating power of these mixed flames may be explained by considering the carbon particles in an oil flame as radiators. These particles also exist in the mixed flame. The heat generated in burning the gas heats the carbon particles by conduction, and they in turn radiate heat to the surroundings.

Lobo and Evans[10] have made a complete study of petroleum heaters and the Wilson, Lobo, and Hottell radiation equation [Eq. (79)]. They also present a theoretical equation that appears to check well with all types and arrangements of heaters. With regard to Eq. (79), they conclude that it may be used for designing conventional box-type heaters (Figs. 133*a*, 133*c*, 134) but subject to the following qualifications:

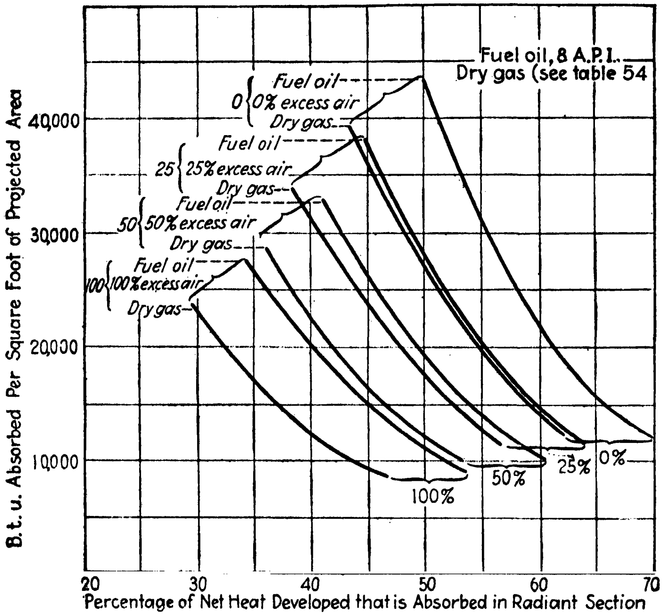

FIG. 137.—Rate of radiant absorption in simple stills with no recirculation or air preheat.

1. Fuel oil or cracked refinery gas must be used as fuel.
2. Radiant rates must range between 5000 and 30,000 B.t.u. per hour per square foot based on outside tube area.
3. Percentage of excess air must range between 5 and 80 per cent.
4. Tube skin temperatures must not be closer than 400°F. to the temperature of the flue gas leaving the radiant section.
5. Length of radiant beam should be greater than 15 ft.

The theoretical equations developed by them give much closer results (maximum 16 per cent deviation), but the use of the equations is complicated, particularly for design purposes.

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[10] Heat Transfer in the Radiant Section of Petroleum Heaters, *Trans. Am. Inst. Chem. Eng.*, **35**, 743 (1939).

Various types of elaborate burner systems for the production of more radiation and a better distribution of heat in the combustion chamber have been suggested. Some of these consist of a furnace floor of small gas jets; and although they perform well, they are expensive. A successful artificial-radiation device is the muffle burner of the Alcorn Combustion Company. In this burner the gas fuel is fired through a long muffle which may extend along the entire length of the floor of the still. The muffle becomes hot and acts as a radiator, and the flame that issues from the end of the muffle also contributes to the radiation.

Example 66. Rate of Absorption in the Radiant Section.—A pipestill uses 500 lb. per hr. of an oil fuel (net heating value 17,500). The radiant section has 156 sq. ft. of projected area, and the tubes (4 in., outside diameter) are spaced at a center-to-center distance of 8 in. There are two rows of tubes in the radiant section. The ratio of air to fuel is 17.9 (30 per cent excess air). What percentage of the heat liberation is absorbed in the radiant section, and how many B.t.u. are absorbed per hour through each square foot of projected tube area?

$$Q = 500 \times 17,500 = \text{heat liberation} = 8,750,000$$

$$a = 0.98 \text{ (Fig. 136)}$$

$$R = \frac{1}{1 + \frac{17.9\sqrt{8,750,000/0.98 \times 156}}{4,200}} = \frac{1}{1 + \frac{17.9 \times 240}{4,200}} = \frac{1}{2.02} = 0.495$$

$$\text{Heat absorbed in radiant section} = 8,750,000 \times 0.495 = 4,330,000$$

$$\text{B.t.u. absorbed per sq. ft. of projected area} = \frac{4,330,000}{156} = 27,700 \text{ per hr.}$$

The results may be checked by the use of Fig. 137. Reading up from 49.5 on the base to the 30 per cent excess air line for an oil fuel, the rate of absorption is estimated as 27,000 B.t.u.

Commercial Radiant Rates.—The radiation rates that should be used in pipestills cannot be given as definite figures because of the many factors that appear in commercial operation. Among these are the wide variety of stocks, the variation in the liquid velocity, and the different temperatures that are used for the different stocks. However, Table 63 presents rates that have been used in commercial plants. Doubtless many stills deviate from the recommendations in the table. With carefully designed stills in which local overheating is avoided, much higher rates can be maintained. Rates of 45,000 B.t.u. per square foot of projected area have been used in commercial cracking furnaces of the type shown in Fig. 134 for the simple heating zones, but such a rate is too high for the cracking or soaking zone.

TABLE 63.—RADIATION RATES

Service	Radiant absorption rate, B.t.u. per sq. ft. projected area	Radiation factor (25 per cent excess air). No preheat or recirculation	Usual oil velocity, ft. per sec. at 60°F.	Radiant absorption rate, B.t.u. per sq. ft. outside surface*
Topping crude oil	31,000	0.48	3	9860
Reduced crude, vacuum	25,500	0.51	4	8110
Cracking (outlet in convection)	25,500	0.51	5	8110
Rerunning pressure distillate	25,500	0.51	4	8110
Cracking (outlet in radiant)	17,000–10,000	0.57–0.66	6	5410–3800
Rerunning lubricating oils:				
a. Light oils (pressed dist.)	20,000	0.55	5	6370
b. Heavy oils (bright-stock sol.)	17,000	0.57	7	5410

* Rate on projected area divided by 3.1416.

Distribution of Radiant Heat.—In designing the details of a pipestill or in designing a still for a special service, a knowledge of the distribution of radiation in different parts of the radiant section is important. Usually only two rows of radiant tubes are used in the radiant section. If three tubes are used, the third row receives only about 12 per cent as much heat as the first row, and hence a third row is of little value. Many stills have been built with only one row of tubes.

The first rows of tubes in the convection section also absorb heat by radiation from the flame as well as heat by convection. The radiation into the convection section, if the tubes are not screened by superheater tubes or by brickwork, is about as follows: first row, 100 per cent; second row, 56 per cent; third row, 19 per cent; fourth row, 4 per cent; and fifth row, 1.5 per cent.

The first convection tubes must withstand a more severe rate of heat absorption than any other tubes in the still. Not only do these tubes absorb more heat by convection than any other tubes in the convection section, but they also receive heat by radiation. Often the first row of convection tubes absorbs

18,000 B.t.u. per square foot of outside surface (11,000 B.t.u. by radiation and 7,000 by convection). This is a rate far higher than those suggested in Table 63. For this reason the first rows of the convection section are often designed with the same diameter as the radiant tubes or, in other words, for a high oil velocity. Steam superheater tubes are often placed between the radiant and convection sections to protect the first convection tubes. In a superheater the high rate of absorption is desirable if the superheater is constructed of an alloy steel that can withstand high-temperature oxidation.

The rate of radiant absorption varies at different parts of the radiant section. In ordinary stills the exact distribution of radiation is not important; but for (1) heating sensitive stocks such as treated lubricating oils, (2) heating to very high temperatures as in cracking stills, and (3) heating two different stocks in separate coils in the same radiant section, the rate of heat absorption in the different parts of the furnace box becomes very important. Data on several stills have been reported that indicate radiation rates that varied by 400 per cent in different parts of the radiant section.

The following method (Example 67) of estimating the distribution of radiant heat is not based on extensive theoretical considerations, but it does give results that were dependable in all instances studied. Radiation proceeds in all directions from point sources within the flame. It proceeds in straight lines and either strikes a cold tube surface and is absorbed or strikes a refractory wall. Upon striking a wall, the radiation first heats the wall; but after the wall reaches a temperature higher than that of the tubes, the wall itself begins to radiate. At the high temperature existing in pipestill walls, the walls act as reflectors so that radiation falling upon the wall is reflected in such a way that the angle of reflection equals the angle of incidence. Each time the radiation is reflected, it becomes less intense, (1) owing to the heat lost through the walls by conduction and (2) because the intervening gas is heated. The intensity of reflected radiation, with the heat liberated considered as unity, is somewhat as follows: initial radiation, 0.75; once reflected, 0.68; twice reflected, 0.61; and thrice reflected, 0.54. The way in which this information can be used is shown in Example 67.

Example 67. Distribution of Radiation in Radiant Section.—A scale drawing of the inside of a commercial furnace is shown in Fig. 138. The distribution of radiation can be determined graphically by selecting a source of radiation in about the center of the flame and dividing the total radiation into equal parts. Thirty-five equal units or rays of radiation are used in this example. Only 9 rays are shown in Fig. 138 because if 35 are shown such a maze of lines results that the drawing is not intelligible.

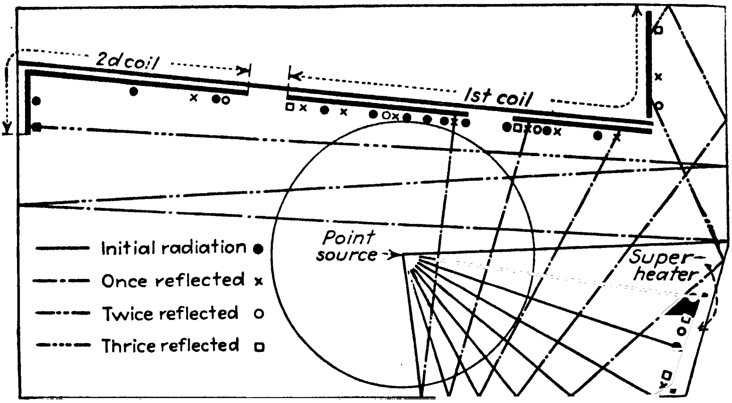

FIG. 138.—Distribution of radiation in radiant section. Refer to Example 67.

The 35 lines or rays were completed as for the 9 shown in Fig. 138. Upon the first coil fall 9 rays of initial radiation; 8 rays of once-reflected radiation; 3 rays of twice-reflected radiation; and 3 of thrice-reflected radiation. The total radiation (comparative units only) that is absorbed by the first coil is

Initial	9 × 0.75 =	6.0
Once reflected	8 × 0.68 =	5.44
Twice reflected	3 × 0.61 =	1.83
Thrice reflected	3 × 0.54 =	1.62
	Total radiation to first coil =	14.89

There were 88 sq. ft. in the first coil so that the relative radiation per square foot is

$$\frac{14.89}{88} = 0.1695$$

The average relative rate per square foot for all of the radiant surface was 0.126 (see tabulation, p. 445), and the actual average absorption rate was 11,000 B.t.u. per sq. ft. of projected area per hr. Hence the rate in the first coil is

$$\frac{0.1695}{0.126} \times 11{,}000 = 14{,}800 \text{ B.t.u.}$$

The same computations for each of the three coils are shown in the following tabulation:

	Relative heat units absorbed by		
	First coil	Second coil	Super-heater
Initial radiation (No. rays × 0.75)	6	2.25	1.5
Once reflected (No. rays × 0.68)	5.44	1.36	0.68
Twice reflected (No. rays × 0.61)	1.83	0.61	0.61
Thrice reflected (No. rays × 0.54)	1.62	0	1.08
Total heat units for each coil	14.89	4.22	3.87
Surface in each coil (sq. ft.)	88.0	71.0	23.0
Relative absorption rate, heat units per sq. ft.	0.1695	0.0595	0.168

$$\text{Relative ave. absorption rate} = \frac{14.89 + 4.22 + 3.78}{88 + 71 + 23} = 0.126$$

Actual ave. absorption rate = 11,000 B.t.u. per sq. ft.

Actual rates:

$$\text{First coil} \ldots\ldots \quad 11{,}000 \times \frac{0.1695}{0.126} = 14{,}800$$

$$\text{Second coil} \ldots\ldots \quad 11{,}000 \times \frac{0.0595}{0.126} = 5{,}100$$

$$\text{Superheater} \ldots\ldots \quad 11{,}000 \times \frac{0.168}{0.126} = 14{,}750$$

The accuracy of the method can be improved by repeating the foregoing computations for several planes and for several point sources of radiation.

CONVECTION

The rate of heat absorption in the convection section can be approached with more assurance than for the radiant section. The only troublesome points are (1) the combination of radiation and convection heating that occurs through the first rows of the convection section and (2) the radiation from the hot gas and the walls of the convection section. The first difficulty is often handled by counting these tubes twice; *i.e.*, the first two rows are counted as radiant tubes, and they are also counted as convection tubes. The second difficulty is discussed later.

The empirical equation by Monrad[11] is the only comprehensive formulation of convection transfer rates. For pipestills he suggests

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[11] Heat Transmission in Convection Sections of Pipestills, *Ind. Eng. Chem.*, **24**, 505 (1932).

$$h_c = \frac{1.6G^{0.667}T^{0.3}}{D^{0.33}} \tag{80}$$

where h_c = pure convection film transfer rate for flue gas flowing at right angles to staggered tubes (no radiation).
G = mass velocity of gas at minimum cross section, lb. per sec. per sq. ft.
T = average gas temperature, deg. F. abs.
D = tube diameter, in.

Equation (80) applies to any conventional arrangement of the convection section. However, the coefficient h_c is the pure convection coefficient, and it does not include radiation from the flame, from the hot gas, or from the walls. Monrad[11] has made a study of these factors. The first of these is designated as h_{rg} or the coefficient of heat transfer from the gas by radiation. As an approximation, the value of the gas radiation coefficient may be found by the following relation:

$$h_{rg} = 0.0025T - 0.5$$

where T is the average temperature in degree Fahrenheit of the flue gas. More exact methods of computing this factor are given in the aforementioned reference.[11]

The second factor, the wall effect, ranges in magnitude between 6 and 15 per cent of the sum of the pure convection and the radiation coefficients.

$$\text{Per cent wall effect} = \frac{h_{rb} \times A_w \times 100}{(h_c + h_{rg} + h_{rb})A_t}$$

where h_{rb} = radiation coefficient from walls = $0.00688p(T/100)^3$.
p = emissivity of wall surface, usually about 0.95.
T = absolute temperature of tube, deg. R.
h_c = pure convection coefficient (Eq. 80).
h_{rg} = gas radiation coefficient.

Subscripts w and t refer to the wall and tube respectively. The complete coefficient of heat transfer in the convection section may be computed from the preceding items as follows:

$$h = \left(\frac{100 + \text{per cent wall effect}}{100}\right) \times (h_c + h_{rg}) \tag{81}$$

In addition, the first convection tubes receive radiation directly from the furnace, but this additional heat may be better considered as a part of the radiant section.

A tabulation of approximate total transfer coefficients is given in Table 64.

TABLE 64.—APPROXIMATE CONVECTION COEFFICIENTS

Velocity, ft. per sec.	Temperature, deg. F.	Size of tube (O.D.), in.		
		2	4	6
9	800	6.9	5.8	5.3
9	1000	7.2	6.2	5.6
9	1200	7.5	6.6	6.0
9	1400	7.8	6.9	6.4
12	800	8.0	6.7	6.1
12	1000	8.2	7.0	6.4
12	1200	8.5	7.3	6.7
12	1400	8.8	7.7	7.1
15	800	9.0	7.5	6.8
15	1000	9.2	7.8	7.1
15	1200	9.4	8.1	7.4
15	1400	9.7	8.4	7.7

The area through which heat is transferred may be considered as the outside area of the tubes because the gas film coefficient controls. The resistances that are due to the oil film and the metal wall are so small that they are usually negligible. The gas velocity seldom exceeds 15 ft. per second in stills that are dependent on a stack for draft. A stack draft of 0.6 in. of water will cause a velocity of about 15 ft. per second. At low capacities the velocity may be only 10 ft. per second, but in recirculation stills the velocity may exceed 25 ft. per second.

Air preheaters are of many designs. Little data on the transfer rates are available. However, the rates are low because two gas films are present and because little radiation occurs. The rate probably ranges between 2 and 4 depending upon the velocity.

Pipestill Losses.—The heat losses in pipestills, when based on the net heating value, consist mainly of two items: (1) the sensible heat content of the stack gases above 60°F. and (2) the losses through the furnace walls, header boxes, roof, floor, etc. Pipestills are usually fired with 25 per cent or more excess air, and hence carbon monoxide is seldom reported in the flue gas, and no loss occurs by incomplete combustion of the fuel. No loss due to the heat contained in the cinder or combustible in the cinder is necessary unless coal is fired.

The brickwork of pipestills and boilers is not usually airtight. The following tabulation shows the flue-gas analysis at two points in a commercial still.

Flue gas	Radiant section	Breeching
Carbon dioxide	13.5	7.6
Oxygen	0.7	9.4
Carbon monoxide	0.3	0.0

Air leaked into the still in the radiant and convection sections and lowered the percentage of carbon dioxide. In this still, radiation occurred at a low percentage of excess air but the stack loss was for a high percentage of excess air.

The stack loss may be rapidly computed by referring to Figs. 56 and 57 (Chap. XI), but the method outlined in Example 32 should be used for exact computations. In making a detailed heat-balance, the steam that is required to atomize the oil is easily forgotten.

Actual plant data on the losses through walls, headers, roof, etc., of a pipestill will be discussed. The temperatures[12] on the outside of the furnace were as follows:

The walls were constructed with 13½ in. of refractory brick, 4½ in. of insulation brick, an average sealed air space of 1 in., and

Surfaces	Average surface temp., deg. F.	Air temp., deg. F.
Refractory walls, etc.:		
Shady end	140	70
Sunny end (slight breeze)	158	72
Shady side (between headers)	132	69
Sunny side (between headers, breezes)	183	72
Steel walkways and supports	105	69 and 72
Surface of suspended roof tile	323	173
Header boxes, etc.:		
Shady side	230	69
Sunny side (breezes)	261	72

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[12] These temperatures were obtained by pressing a thermometer against the surface by means of a piece of dry loose asbestos. Such temperatures are low, but in this case a correction was determined by measuring known temperatures by the same method.

covering of cement board $\frac{1}{4}$ in. thick. Inasmuch as the temperatures were higher on the sides exposed to the sun and the air temperature is not appreciably raised by the sun, the most dependable surface temperatures are those of the shady walls.

From the foregoing data and the natural-convection rates as given by Eq. (28), the following losses were computed (Table 65):

TABLE 65.—LOSSES FROM PIPESTILL WALLS

Surfaces	Wall temp.	Air temp.	Surface, sq. ft.	ΔT	h_g	Loss, B.t.u. per hr.
Refractory walls....	136	69	1,632	67	1.92	210,000
Header boxes, etc...	230	69	640	161	2.43	250,000
Roof..............	323	173	1,020	250	2.96	755,000
Exposed steel.......	105	69	80*	36	1.71	5,000
Floor*.............	...	...	......	...	....	180,000*
Total............	...	...	......	...	....	1,400,000

* Estimated.

At the time of this test, the still was developing 26,500,000 B.t.u. per hour so that the radiation losses were approximately

$$\frac{1,400,000}{26,500,000} \times 100 = 5.3 \text{ per cent}$$

This is a reasonable loss for stills operating in dry weather with a normal movement of air. For carefully built stills the loss from the radiant section may be considered as 3 per cent and from the convection section 2 per cent.

Example 68. Design of Pipestill.—Thirty thousand pounds of oil per hour is to be heated from 300 to 700°F., vaporizing about 66 per cent of the oil. About 10,000,000 B.t.u. per hr. is required for this service. A radiant-absorption rate of 20,000 B.t.u. per hr. per sq. ft. of projected area is advisable. An efficiency of 75 per cent is satisfactory. The fuel oil has a net heating value of 17,600 B.t.u. per lb. and produces 14.7 lb. of flue gas if burned with no excess air. Twenty-five per cent excess air will be used in the design calculations.

The pounds of air (no excess) per pound of fuel is $14.7 - 1 = 13.7$.

Tables 25 and 62 indicate that this fuel will have radiant properties between a heavy oil fuel and natural gas.

Figure 137 shows that the percentage of the total heat liberation that will be absorbed in the radiant section will be about 53.5.

If wall losses of 3 and 2 per cent are adopted for the radiant and convection sections, the heat-balance can be set up as follows:

	Per cent	B.t.u.
Efficiency (given)	75	10,000,000
Heat in fuel (heat liberation)	100	13,330,000
Radiant section loss	3	400,000
Convection section loss	2	260,000
Stack loss (25–3–2)	20	2,670,000
Radiant absorption	53.5	7,140,000
Convection absorption (75–53.5)	21.5	2,860,000
Total	100.0	13,330,000

Radiant section:

$$\text{Radiant surface} = \frac{7{,}140{,}000}{20{,}000} = 357 \text{ sq. ft. (projected)}$$

If 3- by 4-in. tubes are used, the length of the effective radiant tubing is

$$\frac{357}{0.33} = 1{,}070 \text{ ft.}$$

Convection section: The temperature of the stack gas is 810°F. (Fig. 56). The temperature of the gas as it enters the convection section can be obtained from the same figure. The heat that remains in the gas as it leaves the radiant section is

$$100 - 53.5 - 3 = 43.5 \text{ per cent}$$

At 43.5 per cent (Fig. 56) the temperature is 1700°F. (This high temperature indicates that more excess air should be used unless some decomposition can be tolerated.)

The temperature of the oil as it enters the convection section is 300°F., and the temperature at which it leaves can be computed as follows:

$$2{,}860{,}000 = 30{,}000\ (t - 300)\ 0.6$$
$$t = 460°\text{F.}$$

The logarithmic mean temperature difference between the flue gas and the oil is

$$\frac{(1{,}700 - 460) - (810 - 300)}{\log_e \dfrac{1{,}700 - 4{,}600}{810 - 300}} = 825$$

The transfer rate can be estimated from Table 64. At a velocity of 12 ft. per sec. and an average temperature of 1250°F. the transfer rate for 3- by 4-in. tubes is about 6.95.

$$\text{Convection surface} = \frac{2{,}860{,}000}{6.95 \times 825} = 500 \text{ sq. ft. outside surface}$$
$$\text{Length of tubing} = 477 \text{ ft.}$$

The total effective length for radiant and convection sections is 1,070 plus 477, or 1,547 ft.

Recirculation and Air Preheat.—Many claims have been made for the recirculation type of pipestill. In part these claims are justified, but often they lead to misconceptions. The important advantages of the recirculation still are as follows: (1) The rate of radiant absorption can be controlled by adjusting the quantity of flue gas that is recirculated, and (2) a low rate of radiant absorption can be obtained without building an excessively large radiant section. If the duty of an ordinary still is increased to above its rated capacity, the rate of absorption in the radiant section increases greatly and all out of proportion to the increase in the duty. In the recirculation still the rate of absorption can be kept low by increasing the circulation of flue gas. In both types of stills the efficiency may decrease slightly, but the efficiency of pipestill heaters is not of major importance to the refiner. The most real concern of the refiner is to avoid deposits of coke with resulting costly shut-downs and to avoid discoloration of finished stocks by localized overheating. The absorption rate can be regulated in ordinary stills by using different quantities of excess air, but a great loss in the efficiency occurs if the absorption rate is lowered by even a few thousand B.t.u.

In general, recirculation stills require less surface than simple stills of the same efficiency.[13] However, the saving in the cost of surface must pay for the recirculation equipment, the gas-tight construction of the still, and the increased operating cost. Thus the initial cost is usually greater for the recirculating still, as well as the operating cost, so that the adoption of a recirculating still rests entirely with the advantage that it affords as a means of controlling the rate of radiant heat absorption. In the past the design of pipestills for low radiant-absorption rates was not well understood and the recirculation still was widely used. Today the industry is reverting to the use of simple radiant-type stills that are designed for a specific service.

Table 66[13] indicates the effect of flue-gas recirculation. Still 1 was designed for no recirculation, an efficiency of 75 per cent, and a radiation factor of 0.5. Stills 2 and 3 are the same still as No. 1 except that flue gas was recirculated. The comparison is hardly fair because a recirculation still should be built with more convection surface. Hence stills 4, 5, and 6 are compared

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[13] Nelson, W. L., Modern Pipestill Heater Design, Recirculation, *Petroleum Eng.*, June, 1933, p. 23.

TABLE 66.—COMPARISON OF RECIRCULATION AND SIMPLE STILLS

Absorption 10,000,000 B.t.u. per hr.
4- by 5-in. tubes.
15 ft. per sec. flue-gas velocity in the simple stills.

Stills 1, 2, and 3, radiant surface, 266 sq. ft. proj.
convection surface, 540 sq. ft. (O.D.)
Stills 4, 5, and 6, radiant surface, 119 sq. ft. proj.
convection surface, 570 sq. ft. (O.D.)

Still No.	Recirculation	Duty ÷ 10^6		Convection section				Radiant section			Eff.	Length of tubing	Length of tubing for simple still*
		On fuel	On Q or on heat developed	In, deg. F.	Out, deg. F.	Mean temp. diff., deg. F.	h	Factor on Q	Per cent of heat in fuel	Absorption rate			
1	0 – 1	13.3	13.3	1680	810	810	7.6	0.5	50	25,000	75	1,055	1,055
2	0.5 – 1	13.3	14.7	1630	810	800	9.5	0.40	44	22,100	75	1,055	1,105
3	1 – 1	13.1	15.4	1540	780	750	12.0	0.325	38	19,000	76	1,055	1,204
4	0 – 1	13.3	13.3	2100	810	975	8.4	0.40	40	44,700	75	720	720
5	0.5 – 1	13.3	14.7	1930	810	915	10.8	0.311	34	38,500	75	720	746
6	1 – 1	13.3	15.8	1700	810	845	12.3	0.24	29	32,500	75	720	802

* Nonrecirculation stills designed for the same radiant absorption rate as the corresponding recirculation stills.

in the same manner except that the nonrecirculation still 4 was designed for a radiant factor of 0.4. All of the stills were designed for an absorption of 10,000,000 B.t.u. per hour, the use of 25 per cent excess air, and heating a crude oil stock from 300 to 700°F. The last column in Table 66 shows the surface required to get the same radiant factor as with recirculation but without recirculation of flue gas.

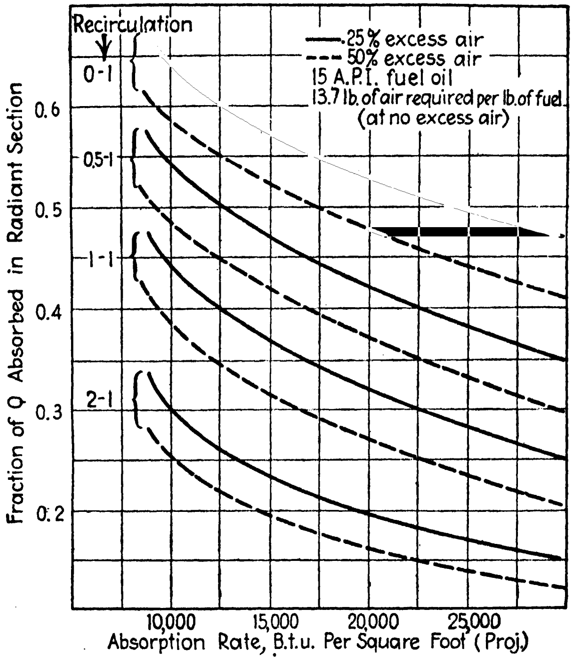

FIG. 139.—Radiant-absorption rate when recirculating flue gas.

Examination of Table 66 shows essentially no difference between simple and recirculation stills except the rate of absorption in the radiant section. Recirculation stills usually appear to more advantage than shown in the table because the convection section can be arranged for higher gas velocities than those used in computing Table 66.

The effect of recirculation on the rate of radiant absorption is shown graphically in Fig. 139. In studying recirculation stills the exact definition of the radiation factor R [Eq. (79)] must be kept clearly in mind. This factor is the fraction of the total heat, developed in the flame, that is absorbed in the radiant section. Thus, in simple stills, *R* is the fraction of the heat contained in the fuel, whereas in circulation stills or air preheat stills it is the fraction of the total heat liberated in the flame; this total may consist of the sum of the heat in the fuel, the heat in the recirculated gases (above 60°F.), and the heat in the air (above 60°F.).

Air preheat increases the flame temperature and the rate of radiant absorption so that it tends to defeat the advantage of flue-gas recirculation. Higher efficiencies can be obtained by air preheat, but the same efficiency can be obtained at about the same expense by building a larger convection section in the still. However, the burners can be more exactly adjusted if the primary air is under a slight pressure as in a preheat system.

Pressure-drop.—To a large extent the pressure loss that occurs by friction in the tubes of a pipestill must be estimated by resorting to plant experience. Fair results can, however, be attained by the general method outlined on page 257. Pressure-drops computed by this method are shown in the following tabulation.

Material	Pressure-drop, lb. per sq. in.	
	Actual	Computed
Crude oil	198	192
Reduced crude oil	124	115
Brightstock solution	197	209
Treated cylinder stock	85	103
Distilled cracking-stock	605	563
Distilled cracking-stock	394	362
Distilled cracking-stock	238	275

Tube Design.—The temperature difference that always exists when heat is delivered through a series of resistances becomes of great importance in the selection of pipestill tubes. Nearly all of the radiation that falls upon a tube must be absorbed, regardless of the transfer rate on the inside of the tube. The transfer of heat through the oil film is a conduction phenomenon, and hence a difference in temperature must exist between the main body of oil and the tube wall. Thus the temperature in the film and tube is higher than in the fluid.

Solid coke may be deposited because of the high temperature in the oil film. As coke is deposited, the temperature in the tube rises, and it continues to rise as coke is deposited until finally the tube attains the temperature of the furnace or it bursts. For normal thicknesses of coke, the amount of heat absorption is not decreased greatly. Partridge and White[14] find that a normal thickness of boiler scale does not decrease the rate of radiant heat absorption by more than about 3 per cent. In general, coke deposits act in the same manner.

Pipestill tubes often receive radiation at the rate of about 5500 B.t.u. per square foot per hour of outside surface or a rate of about 9500 B.t.u. per square foot of inside surface. The velocity of the oil is usually such that the film transfer rate is about 200 B.t.u. per square foot per hour per degree of temperature difference. Obviously the temperature difference through the oil film, if the tube is clean, is

$$\frac{9{,}500}{200} = \frac{\dfrac{\cancel{\text{B.t.u.}}}{\cancel{\text{Hr.}} \times \cancel{\text{Ft.}^2}}}{\dfrac{\cancel{\text{B.t.u.}}}{\cancel{\text{Hr.}} \times \cancel{\text{Ft.}^2} \times {}^\circ\text{F.}}} = 47.5^\circ\text{F.}$$

If the oil temperature is 900°, the temperature at the inside of the wall is (900 + 47.5) or 947.5°F. If the wall is ½ in. thick, the temperature drop in the wall will be

$$\text{Deg. drop in wall}^{15} = \frac{9{,}500}{25} \times \frac{0.5}{12} = 15.8$$

and the outside of the metal tube is at (900 + 47.5 + 15.8), or 963.3°.

If a ⅛-in. coke deposit having a conductivity of 0.5 is produced, the tube temperature is increased by

$$\frac{9{,}500}{0.5} \times \frac{0.125}{12} = 198^\circ\text{F.}$$

and the outside tube temperature is

$$900 + 47.5 + 198 + 15.8 = 1161.3^\circ\text{F.}$$

These temperatures are shown in Fig. 140.

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[14] The Effect of Boiler Scale, *Ind. Eng. Chem.*, **21**, 839 (1929).

[15] Conductivity of steel is about 25 B.t.u.

A temperature of 1160° (red heat) is too high for a carbo steel tube because the strength drops to about 1,000 lb. per squar inch (creep strength) and the tube will fail. However, if th pressure is very low so that the coke can be deposited to thicknesses greater than ⅛ in., the tube wall temperature continues to rise with increase in coke thickness and eventually the tube will attain the temperature of the furnace. At this stage the furnace must be fired harder, the temperature in the tube increases proportionally, the pressure-drop increases rapidly, and eventually the tubes become plugged or they fail.

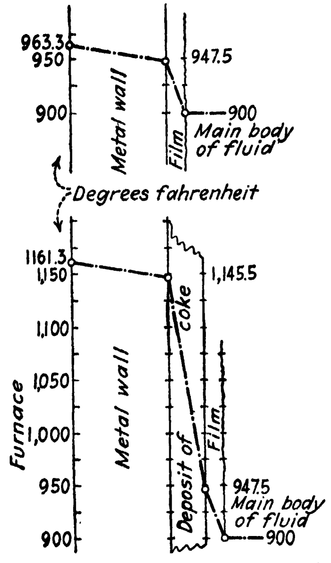

FIG. 140.—Effect of coke on wall temperature.

The rate of coke deposition is not greatly dependent on the amount of coke already deposited, but the rate can be retarded by increasing the velocity or the transfer rate through the oil film. The rate of depositing coke is directly dependent on the thickness of the oil film because the thicker the film the greater the volume of oil (in the film) that is exposed to the high temperature. Thus the rate of coke deposition will be related to the transfer rate and the temperature in the film. Figure 141 shows the relative rate of coking for different film transfer rates and for common rates of total heat absorption. They are based on a rate of unity for a transfer rate of 300 and an absorption rate of 10,000. These conditions are commonly found in cracking plants. The data are only approximate because the velocity and the film transfer rate cannot be accurately computed. Only two factors were accounted for in computing Fig. 141; one, the temperature in the film and the way that it affects the rate of cracking, and the other, the thickness of the film.

Figure 141 clearly shows why a hot velocity exceeding 13 ft. per second is now commonly used in cracking plants. A higher velocity greatly increases the pressure-drop and aids little in

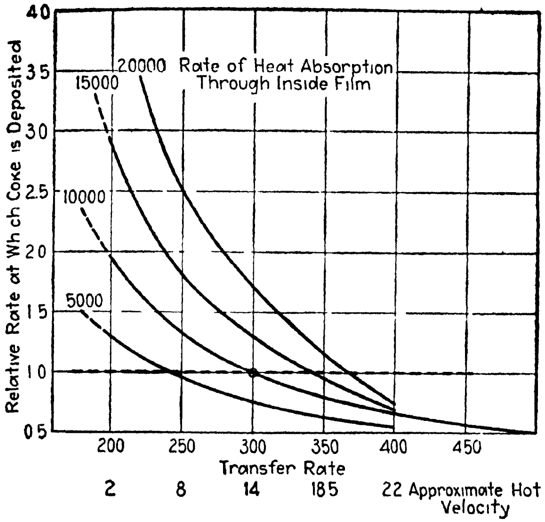

FIG. 141 —Approximate relative rate of coke formation

FIG 142 —Steel structure of pipestill. (*A. J. Smith Engineering Company*)

decreasing the formation of coke. Absorption rates of 10,000 to 13,000, through the inside surface of the tube, are widely used. In topping plants the temperature in the main body of oil is much lower and hence Fig. 141 does not apply.

Tube thicknesses are usually determined by means of the A.S.T.M. formula that follows, but an additional thickness of 0.1 to 0.25 may be added to care for thinning by corrosion.

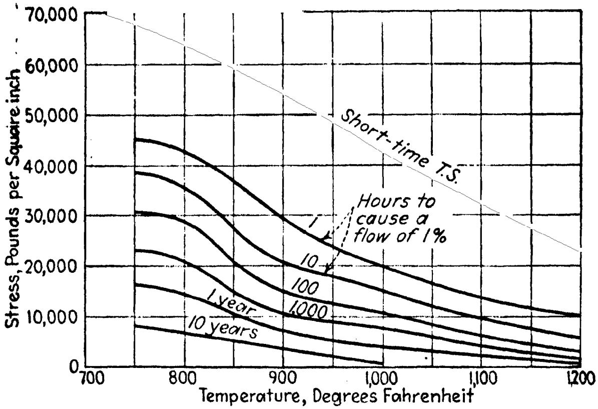

FIG. 143.—Rate of flow of cast carbon steel at elevated temperatures. (*Kanter and Spring, American Society for Testing Materials.*)

$$t = \frac{d(P + 250) + 0.0785}{2(S - P - 250)}$$

where t = thickness of tube wall, in.
P = internal pressure, lb. per sq. in.
d = internal diameter, in.
S = working strength of steel (creep strength), lb. per sq. in.

A thorough study of the stresses in thick-walled cylinders under conditions of creep and while heat is being transferred has been made by Bailey[16] and by Rhys.[17]

Materials for High Temperatures.—The common method of measuring the strength of metals at high temperatures is by long-time heating tests. Short-time tests are unsuccessful because in a furnace the metal stretches or creeps as time progresses and will fail under a load that appears to be safe by short-time tests. The effect of time on the strength of cast carbon steel is shown in Fig. 143.[18] The creep strength or creep limit may be defined as the load (pounds per square inch) that a material can withstand at a high temperature without exceeding a given rate of stretch. Creep strengths are frequently given as the pounds per square inch that will not cause an elongation of more than 1 per cent in 10,000 hr. A creep of 1 per cent in 100,000 hr. has also been

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[16] BAILEY, R. W., The Utilization of Creep-stress Data in Engineering Design, *Proc. Inst. Mech. Eng.* (London), 1935.

[17] RHYS, C. O., Application of Bailey's Theory of Tube-stress Calculations, *Proc. A.P.I., Div. Refining*, 1938, p. 102.

TABLE 67.—PROPERTIES OF TUBE STEELS

Kind of steel	Approximate composition			Design* strength, lb. per sq. in.	Relative penetration by scaling	Relative cost (1940)
	% Cr	% Si	% Mo			
Killed carbon	0	0.2	0	4,000	1.0	1.0
Carbon molybdenum	0	0.3	0.5	12,000	1.13	1.5
Silicon molybdenum	0	1.5	0.5	6,400	0.73	1.6
1 chromium, silicon, molybdenum	1.0	1.25	0.5	8,000	0.84	1.9
1.25 chromium, silicon, molybdenum	1.25	0.75	0.5	18,000	0.77	1.9
2 chromium, molybdenum	2.0	0.5 max.	0.5	9,300	0.70	2.1
2 chromium, silicon, molybdenum	2.0	1.25	0.5	9,000	0.29	2.2
2.5 chromium, silicon, molybdenum	2.5	0.75	0.5	11,000	0.55	2.4
3 chromium, silicon, molybdenum	3.0	1.25	0.5	9,000	....	2.5
3 chromium, molybdenum	3.0	0.5 max.	1.0	......	0.46	2.7
5 chromium, molybdenum	5.0	0.2	0.5	10,000	0.48	3.3
5 chromium, silicon, molybdenum	5.0	1.5	0.5	9,000	0.06	3.5
5 chromium, silicon, aluminum,† molybdenum	5.0	1.5	0.5	7,600	0.03	3.6
9 chromium molybdenum	9.0	....	1.5	9,000	0.06	5.3
18-8 chromium nickel	18.0	(8Ni)	0	17,000	0.01	11.0

* Based on creep strength at 1000°F. allowing 1 per cent creep in 10,000 hr.

† About 0.7 per cent aluminum.

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[18] STRAUSS, JEROME, *Trans. Am. Soc. Steel Treating*, **16**, 191 (1929).

used in many tests. Table 67 shows pertinent properties of several common tube steels.

Economic studies[19] of the life of tubing materials as a function of strength, cost, and resistance to scaling by high-temperature oxidation indicate clearly that most alloy steel tubes are less expensive to install and operate than plain carbon steel tubes. If sulfide corrosion also occurs, the saving is even greater. The approximate resistance of tube materials to sulfide corrosion is somewhat as follows:

Steel	Relative Penetration (Carbon as 1.0)
Carbon	1.0
Carbon molybdenum	0.61
Manganese molybdenum	0.48
1 chromium	0.58
1.25 chromium, silicon	0.62
2 chromium	0.47
4 chromium	0.36
5 chromium	0.33
6 chromium	0.29
9 chromium	0.23
13 chromium	0.18

The properties of other high-temperature materials that are used in refineries[20] are shown in Table 68.

Egloff and Morrell[21] present the following comparison of return fitting plugs when used in Dubbs cracking stills:

Material	Life before Replacement, Months
Chrome-plated iron	4
Steel	4½–5
Nickel chrome iron	5
Aluminum bronze	1–12
Forged-chrome iron	Over 18
Cast-chrome iron	Over 17
Forged steel	24

Although forged steel will last for a long time, it is not so satisfactory as some other materials because the plugs cannot be easily removed.

[19] NELSON, W. L., Strength and Cost of Alloy and Carbon Steel Tubes, *Oil Gas J.*, June 3, 1937, p. 97; also June 24, 1937, p. 79.

[20] NELSON, W. L., *Oil Gas J.*, Oct. 7, 1937, p. 94.

[21] Safety and Costs Chief Factors in Considering Alloy Steel for Cracking Equipment, *Ref. Nat. Gaso. Mfr.*, April, 1931, p. 77.

TABLE 68.—CHROMIUM ALLOYS FOR HIGH TEMPERATURES

Name	Type of material	Approximate composition, per cent				Working temperature	Relative oxidation resistance*	Service
		Cr	Ni	Si	Others			
Meehanite	Cast iron	0.5	.....	1.3	......	800–1200	....	Convection section castings
Ni Tensyliron	Cast iron	0.5	1–4	1.2–2.7	......	800–1200	....	Convection section castings
Sicromo I	Steel	1.0	0	1.25	0.5 Mo	1000–1200	1.19	Tubes and bends
DM	Steel	1.25	0	0.75	0.5 Mo	1000–1200	1.3	Tubes and bends
Causal metal	Alloy iron	1.5	18–21	2.2	4.5 Cu	900–1300	....	Firebox and still castings
Croloy 2	Steel	2.0	0	0.45	0.5 Mo	1000–1200	1.46	Tubes and bends
Ni Resist	Alloy iron	3.5	14.5	1.5	6 Cu	900–1400	....	Firebox and still castings
4–6 chrome Mo Si	Steel	5.0	0	1.5	0.5 Mo	1000–1300	17.0	Tubes and bends with sulfur corrosion
Croloy 9	Steel	9.0	0	....	1.5 Mo	1000–1300	17.0	Tubes and bends with sulfur corrosion
13 chrome	Steel	13.0	0	....	......	1100–1400	84.0	Cast tube supports
18–8 chrome nickel	Steel	18.0	8	....	......	1100–1400	Very high	Tubes and bends with sulfur corrosion
25–12 chrome nickel	Steel	24–28	10–12	....	......	1300–1800	Very high	Cast tube supports
15–35 nickel chrome	Steel	15.0	35	....	......	1500–2000	Very high	Cast tube supports
Nichrome	Alloy	15.0	60	....	15 Fe	1600–2000	Very high	Instruments, etc.
Nichrome IV	Alloy	20.0	80	....	......	1800–2100	Very high	Instruments, etc.

* Relative to carbon steel taken as 1.0.

Shellstills and Heated Chambers.—The heating of oil in shells or chambers is limited by the amount of heat that can be conducted from the heated surface by means of the boiling oil. In commercial stills the maximum transfer rate is about 6 B.t.u. per square foot per degree Fahrenheit temperature difference per hour, and most stills operate at a transfer rate of about 4. However, if forced circulation is used or internal flues, the rate of transfer may be increased to as much as 12. The temperature difference is the difference between the oil temperature and the gas temperature. Thus the total heat transmission per square foot per hour amounts to about 4000 B.t.u. for an oil at 400°F. to as low as 2000 B.t.u. for an oil at 800°F.

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DENNIS, E. L.: Burners and Their Application, *Ref. Nat. Gaso. Mfr.*, October, 1939, p. 419.

KEY and CLENDENIN: The Necessity of Better Construction of Oil-heating Coils, *Proc. A.P.I., Div. Refining*, 1938, p. 108.

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CHAPTER XXIII

FRACTIONATING TOWERS

In the practical design of petroleum fractionating towers, the principles outlined for two-component systems are of only general value. These principles operate just as surely in the complex-mixture column as in two-component columns, but means of rigorously applying these principles have not been devised. To complicate their application further, petroleum columns are usually operated as multiple-drawn columns; *i.e.*, several products may be withdrawn from the plates intermediate between the top plate and the feed plate. Needless to say, fractionation is not effective at these plates because a part of the vapor that passes them is the overhead or lightest column product, and hence the products that are withdrawn from the intermediate plates must contain some of this low-boiling material. Customarily, the products that are drawn from the side of the tower are separately stripped with steam, in auxiliary stripping columns or stripping sections.

Heat and Material Balances.—Inasmuch as equilibrium methods of determining the reflux are not available, the reflux is universally computed by means of a heat-balance. The vapor-liquid feed enters the tower at a high temperature, and the products are withdrawn at lower temperatures. Hence heat must be removed, and it is referred to as reflux heat. The reflux heat does not consist of sensible heat alone, because the products that are withdrawn as liquids must be condensed. For a particular operation, the reflux heat is an exact quantity of heat, but the heat may be removed in many ways, *i.e.*, by hot, cold, or circulating reflux.

The most satisfactory temperature datum appears to be the vaporizer temperature because this temperature can be accurately estimated and is the temperature about which the entire design of tower and pipestill hinges. By using this datum plane, the heat-balance consists simply of the sensible heat that is required to (1) cool each product from the vaporizer temperature to its withdrawal temperature and (2) condense the products tha are withdrawn as liquids. The reflux that is computed by a heat-balance is the minimum amount by which the process can function. Just enough cooling (by reflux) is provided to cool and condense the products, and hence no reflux flows into the vaporizer section of the tower.[1] At each side-draw plate the internal reflux is depleted by the amount of side-draw product that is withdrawn. The depletion of the reflux as it flows down the column is illustrated in Fig. 144. The dotted lines refer to another manner of withdrawing reflux heat.

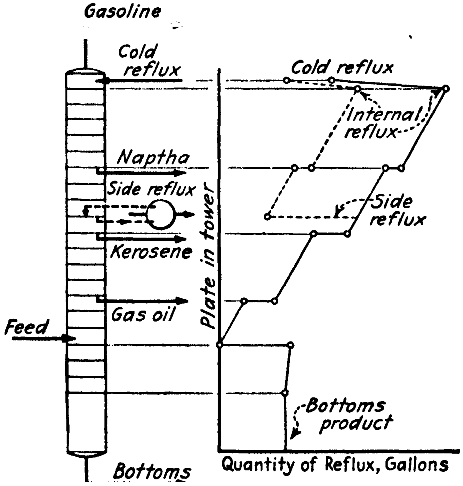

FIG. 144.—Relative amount of reflux or overflow liquid at each tray of a bubble-tower.

Types of Reflux.—The ways of withdrawing reflux heat or the types of reflux are illustrated in Fig. 145. With any of these types, regardless of the volume of liquid reflux, the same quantity of heat is removed. *Cold reflux* may be defined as reflux that is supplied at any temperature below the equilibrium boiling-point of the top product or, more simply, below the temperature of the top of the tower. Each pound of this reflux can remove a quantity of heat, equal to the sum of its latent heat and the sensible heat required to raise its temperature, from the storage-tank temperature to the temperature at the top of the tower. A constant quantity of reflux is recirculated from the product storage tank into the top of the tower. It is vaporized and condensed and returns in like quantity to the product storage tank. This recirculating quantity often amounts to three times the quantity of overhead product.

---

[1] It is always possible to vaporize some of the bottoms product by using a higher vaporizer temperature. This causes some reflux to penetrate to the vaporizer section.

Hot reflux is reflux that is admitted to the tower at the same temperature as that maintained at the top of the tower. Obviously, the reflux or overflow from plate to plate in the tower is essentially hot reflux because it is always substantially at its boiling-point. For convenience, the overflow reflux or reflux in the tower is referred to as *internal reflux*. Both hot and internal reflux are capable of removing only the latent heat, because no difference in temperature is involved. Sometimes five volumes of hot reflux are required per volume of product.

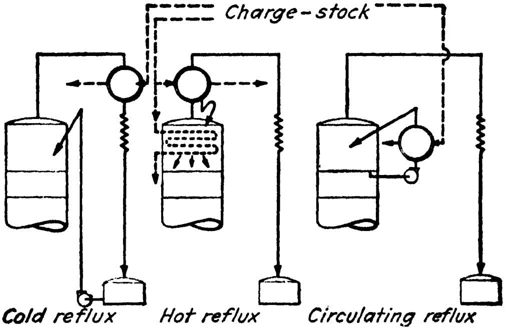

FIG. 145.—Methods of removing reflux heat.

Circulating reflux differs from the foregoing because it is not vaporized. It is able to remove only the sensible heat quantity that is represented by its change in temperature as it circulates. This reflux is withdrawn from the tower as a liquid at a high temperature and is returned to the tower after having been cooled. This type of reflux may be conveniently used to remove heat at points below the top of the tower (side reflux). If used in this manner, it tends to decrease the volume of vapor that the tower must handle. This is illustrated in Fig. 144 by the dotted lines.

Obviously, hot reflux is subject to fluctuations in the quantity and properties of the feed to the plant or to the quantity of cooling agent used, so that it is not entirely satisfactory. In certain cases, when this type is advisable, such as in vacuum-tower systems, the major part of the reflux heat may be removed by hot reflux and cold reflux may be used to remove the rest of the reflux heat. Cold reflux has the advantage of affording an absolute control by means of the reflux pump. Circulating reflux can be controlled in the same manner, but the cost of pumping large quantities of liquid is excessive, and larger heat exchangers are necessary. Regarding the heat that can be saved by heat-exchange, the three systems are comparable, although higher transfer rates can usually be obtained in condensers than in liquid-to-liquid exchangers.

The fact that the quantity of internal reflux flowing from the top plate of the tower is always the same, regardless of the type of external reflux used, is confusing. Vapor arises from the plate below the top and is condensed by the reflux on the top plate. If cold reflux is used, it will take about 2 lb. of vapor to heat and vaporize 1 lb. of cold reflux. Thus 2 lb of internal reflux flow from the top plate for each pound of cold reflux that is admitted to the top of the tower. Similarly, 1 lb. of vapor may deliver enough heat, as it condenses, to heat more than 2 lb. of circulating reflux. In this case, the amount of internal reflux is less than the amount of circulating reflux. When hot reflux is used, the amount of reflux is about the same as the amount of internal reflux.

Example 69. Quantity of Reflux.—A tower-fractionating system is such that 2,000,000 B.t.u. per hr. of reflux heat must be removed. Example 33 illustrates the method of determining the reflux heat. How many pounds and gallons of (1) hot, (2) cold, and (3) circulating reflux are required? Basis: 1 hr.

The overhead product is assumed to be a 58 A.P.I. gasoline (6.22 lb. per gal.). The temperature at the top of the tower is 300°F.

1. *Hot Reflux.*—The latent heat of the gasoline is about 123.

Lb. of hot reflux.............. $\frac{2{,}000{,}000}{123} = 16{,}250$ lb. per hr.

Gal. hot reflux............... $\frac{16{,}250}{6.22} = 2{,}615$ gal. per hr.

2. *Cold Reflux.*—Assume storage tank at 100°F.

Lb. cold reflux......... $\frac{2{,}000{,}000}{123 + (300 - 100)0.575} = 8{,}400$ (Fig. 33)

Gal. cold reflux......... $\frac{8{,}400}{6.22} = 1{,}350$

3. *Circulating Reflux.*—Assume the reflux is cooled from 300 to 200°F.

Lb. circulating reflux........... $\dfrac{2,000,000}{(300 - 200)0.605} = 33,100$

Gal. circulating reflux.......... $\dfrac{33,100}{6.22} = 5,310$

TOWER TEMPERATURES

In making a heat-balance, the temperatures at which the various products are withdrawn from the tower must be determined. These are usually assumed, but the sagacity of these assumptions vitally affects the entire tower design. Hence these temperatures must be as nearly correct as possible. In dealing with a standard design—if there is such a design—the temperatures can be estimated with fair accuracy, but in most cases some factor such as a freak stock, excessive steam quantities, or abnormal pressures connives to introduce great errors into the estimation of these temperatures. The points in Fig. 146 were obtained from commercial operating data, and they show the wide range of tower temperatures that are possible in even the simplest sort of a tower system. Nevertheless, this figure may be used to approximate tower temperatures if great accuracy is not required. Note that this figure is for crude oil topping towers operating with less than 0.6 lb. of steam per gallon of feed-stock.

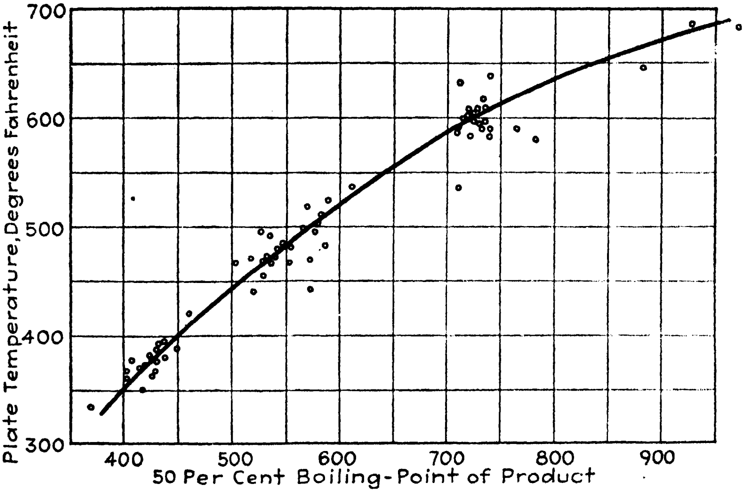

Fig. 146.—Approximate side-draw plate temperatures for topping towers.

Although the following method of determining tower temperatures is open to many criticisms, it does take into account the several variables mentioned above and yields results that are in close agreement with plant data. Table 69 is a tabulation of computed and actual side-draw and top temperatures.

TABLE 69.—TOWER TEMPERATURES

Plant unit No.	Material	Actual temp., deg. F.	Computed temp., deg. F.	Per cent error
Plate temperatures:				
1. Crude, S. Am.	Kerosene	375	367	−2.1
2. Crude, Seminole	Kerosene	374	376	+0.5
3. Crude, Ranger	Kerosene	392	392	
4. Crude, Pa.	Naphtha	335	335	
4. Crude, Pa.	Kerosene	420	417	−0.7
1. Crude, S. Am.	Gas oil	474	473	−0.2
2. Crude, Seminole	Gas oil	469	474	+1.1
3. Crude, Ranger	Gas oil	497	470	+5.4
4. Crude, Pa.	Gas oil	510	519	+1.8
5. Brightstock sol.	Gas oil	450	455	+1.1
8. Cracking, M.C.	Recycle	555	562	+1.3
1. Crude, S. Am.	Wax distillate	600	600	
2. Crude, Seminole	Wax distillate	591	630	+6.6
3. Crude, Ranger	Wax distillate	599	605	+1.0
5. Brightstock sol.	Neutral oil	500	520	+4.0
6. Vacuum, 31 mm.	Cylinder stock	635	625	−1.6
Top temperatures:				
1. Crude, S. Am.	Gasoline	252	268	+6.35
3. Crude, Ranger	Gasoline	256	268	+4.7
4. Crude, Pa.	Light gasoline	243	250	+2.9
5. Brightstock sol.	Naphtha	308	319	+3.6
6. Vacuum, 28.5 mm.	Gas oil and wax dist.	450	452	+0.4
7. Brightstock sol.	Naphtha	308	312	+1.3
8. Cracking, 15 lb. gage	Pressure dist.	390	402	+3.1
9. Crude, Pa.	Gasoline	244	253	+3.7
10. Crude, Pa.	Gasoline	286	287	+0.3

Top Temperature.—Tower temperatures are dependent upon equilibrium vaporization phenomena. The temperature at the top of the tower must be just high enough to cause complete vaporization of the overhead product. A lower temperature will condense a part of the desired overhead product and incorporate it in the first side-draw product, and a higher temperature will cause the inclusion of high-boiling materials which are not desired in the overhead product. If the top of the tower is at atmospheric pressure and no steam is used, the equilibrium vaporization curve of the overhead product will give the top temperature directly. The 100 per cent point on the vaporization curve (see gasoline, Fig. 147) is the lowest temperature at which the overhead product can be a vapor, and this is the top temperature for the simple conditions of a tower operating at a pressure of 760 mm. with no steam. Such a simple case is seldom found, and for normal conditions the top temperature at 760 mm. must be corrected for the tower pressure and for the partial-pressure effect of steam. Example 70 shows how these corrections can be made.

Example 70. Calculation of Top Temperature.—See Fig. 61 (page 197) and Example 33. The top temperatures for hot, cold, and circulating reflux will be computed. This system was actually operated with hot reflux and with circulating reflux, and hence a comparison with the actual temperatures is possible. Tower pressure 780 mm. at the top.

These computations are based on the assumption that the top temperature is measured in the vapor above the top plate. If the temperature was taken in the liquid on the top tray (or one tray down), the temperature would be the same for all types of reflux. Temperatures taken in the vapor line are very erratic because the vapor that leaves the tower is superheated.

A. Hot Reflux.—See the quantities, etc. (Example 33).

Mols reflux:

$$
\begin{array}{lll}
\text{Reflux heat} & = 1{,}860{,}000 \text{ B.t.u. (Example 33)} & \\
\text{L.H. at 286} & = \text{about } 127 & \\
\text{Lb. reflux} & = \dfrac{1{,}860{,}000}{127} & = 14{,}600 \\
\text{Mols reflux} & = \dfrac{1{,}860{,}000}{127 \times 119} & = \quad 123 \\
\text{Mols gasoline} & = \dfrac{3{,}415}{119} & = \quad 28.7 \\
\text{Mols vapor} & = & \quad \overline{151.7} \\
\text{Mols steam} & = {}^{567}/_{18} & = \quad \underline{31.5} \\
\text{Total mols at top of tower} & & = \quad 183.2
\end{array}
$$

According to Dalton's law, the partial-pressure in the gas phase is

$$\frac{151.7}{183.2} \times 780 = 646 \text{ mm.}$$

The initial condensation temperature for the gasoline (100 per cent point on equilibrium vaporization curve) is 296°F. (Fig. 147).

The temperature of 296 corrected to 646 mm. is 284°F.

The *actual* top temperature when using hot reflux was 286°F.

B. Circulating Reflux.—When circulating reflux was used, the top temperature was 244°F. The reflux circulated between 264 and 166°F. The circulating reflux does not vaporize, and hence only the gasoline vapor and the steam need be considered.

Mols gasoline	28.7
Mols steam	31.5
Total mols	60.2

$$\text{Partial-pressure} = \frac{28.7}{60.2} \times 780 = 372 \text{ mm.}$$

Correcting 296 to 372 mm. pressure gives 250°F.

The *actual* top temperature was 244°F.

C. Cold Reflux.—With a lower top temperature (approximately 280°F.) more reflux heat will be required. The heat-balance given in Example 33 is correct except that the sensible heat of the gasoline and of the steam will be different.

Corrections to heat-balance given in Example 33 for a top temperature of 280°F.

		B.t.u.
Gasoline	$3415\,(286 - 280)\,0.485 \times 1.06$	= 10,500
Steam	$567\,(286 - 280)\,0.5$	= 1,700
	Correction	= 12,200

$$\text{Reflux heat} = 1{,}860{,}000 + 12{,}200 = 1{,}872{,}200 \text{ B.t.u.}$$

If the cold reflux is available at 80°F.,

$$\text{Lb. cold reflux} = \frac{1{,}872{,}200}{127 + (280 - 80)0.58} = 7{,}700$$

Mols cold reflux $= \dfrac{7{,}700}{119} =$	64.7
Mols gasoline	31
Mols vapor	95.7
Mols steam	31.5
Total mols	127.2

$$\text{Partial-pressure} = \frac{95.7}{127.2} \times 780 = 587 \text{ mm.}$$

The equilibrium temperature of 296° corrected to 587 mm., gives 277°F.

Side-draw Temperature.—The method of calculating side-draw temperatures is much the same as the calculation of the top temperature except that complications arise because of the presence of the low-boiling materials that pass the draw plate. Furthermore, the equilibrium condensation curve, and particularly the point on this curve that denotes complete condensation, is the basis for computing these temperatures. Flash vaporization and quench condensation are identical phenomena under equilibrium conditions, and hence the 0 per cent point on the flash-vaporization curve is the final condensation point. At this temperature the side-draw product can be completely condensed at 760 mm. pressure if no lighter products or steam are present at the plate.

In practice, steam and vapor of lighter products are usually present, and hence the effect of these vapors on the final condensation temperature must be estimated. The lighter vapors that pass the plate exhibit a wide range of composition. These light vapors extend from materials boiling at almost the same temperature as the side-draw product to materials that are substantially fixed gases. Those vapor materials which are far above their boiling-point behave as fixed gases and lower the condensation point by Dalton's law of partial-pressures just as steam does, but those vapor materials which are at or near their boiling-point are not effective in reducing the partial-pressure. Arbitrarily, the vapors of materials that will be condensed at the second or higher draw plate above the plate under consideration may be considered to act as fixed gases. Also, the vapors constituting the material that is withdrawn from the draw plate above the one under consideration are assumed to have no effect at all on the partial-pressure. Thus in a tower producing gasoline, kerosene, and gas oil, at the gas oil draw plate the gasoline vapor would be considered as a fixed

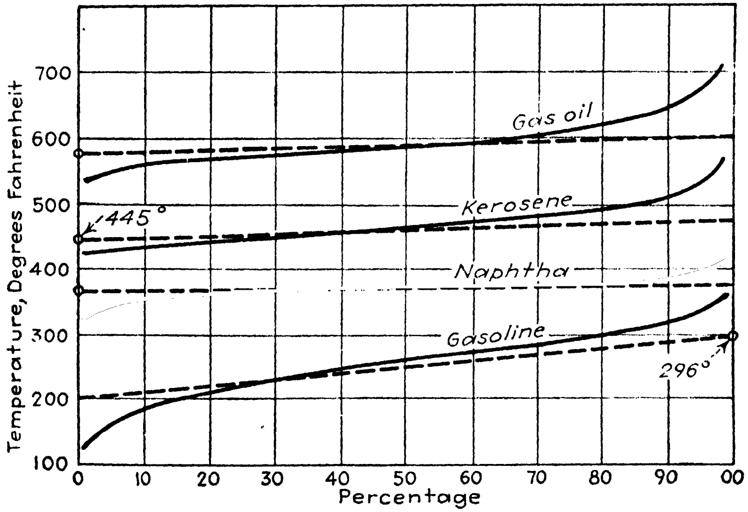

FIG. 147.—A.S.T.M. distillation and flash-vaporization curves of products used in Examples 70 and 71.

gas, whereas kerosene vapor would be assumed to have no effect on the condensation point. This arbitrary classification of vapors appears to be accurate unless the quantity of one of the products is very large or very small. In such a case, the designer can only rely upon judgment. Example 71 illustrates these factors.

Example 71. Calculation of Side Temperatures.—This example is a continuation of Examples 33 and 70. The temperature (420°F.) of the kerosene plate (Fig. 61) will be computed (Envelope II, Fig. 61).

The quantity of reflux heat and reflux (or vapor reflux) that is present on the kerosene plate must be determined. This is computed by making a heat-balance up to the kerosene plate.

Heat-balance to kerosene plate (Example 33):

Cool gasoline vapor	$3{,}415(576 - 420)0.595 \times 1.06$	=	325,000
Cool naphtha vapor	$754(576 - 420)0.59 \times 1.06$	=	73,700
Cool kerosene vapor	$2{,}765(576 - 420)0.58 \times 1.06$	=	265,000
Cool gas oil vapor	$1{,}530(576 - 510)0.592 \times 1.06$	=	63,500
Cool reduced crude liquid	$5{,}610(576 - 510)0.722 \times 1.03$	=	276,000
			1,003,200
Cool steam	$567(535 - 420)0.5$	=	44,000
Condense gas oil	$1{,}530 \times 84$	=	128,500
Condense kerosene	$2{,}765 \times 100$	=	276,500
Reflux heat at kerosene plate			1,452,000

$$\text{Mols internal reflux} \ldots\ldots \frac{1{,}452{,}000}{195 \times 100} = 74.5$$

The internal reflux contains the kerosene, and hence the kerosene need not be added as a material whose partial-pressure must be reduced.

Mols of materials that act as fixed gases:

Steam	31.5
Gasoline	28.7
Naphtha (no effect one way or other)	....
	60.2
Total mols of vapor	$74.5 + 60.2 = 134.7$

Assume a tower pressure of 950 mm.

$$\text{Partial-pressure at kerosene plate} = \frac{74.5}{134.7} \times 950 = 536 \text{ mm.}$$

The atmospheric complete condensation point is 445°F. (Fig. 147). Correcting this temperature to 536 mm. gives 419°F. The *actual* temperature was 420°F.

The gas oil plate temperature can be computed in a similar manner except that kerosene is considered as an inert material and the gasoline and naphtha both act as fixed gases.

In applying the foregoing method to the design of a fractionating tower, the lowest draw-plate temperature should be computed first. The temperature on the lowest plate is assumed; and after the heat balance is computed, the assumption can be checked. If it is not correct, then a second assumption must be made. Each draw-plate temperature, progressing upward in the tower, is computed by such a trial-and-error method until all of the plate temperatures and the top temperature have been computed.

COLUMN DESIGN

The design and construction of petroleum oil columns are governed largely by empirical methods. So many variables mav affect the performance of a fractionating column that engineers have not been able to study all of them carefully.

Even the thickness of the tower shell and plates is estimated by a consideration of the corrosion that may occur rather than on a consideration of the pressure. The thickness normally ranges from ¼ in. for columns less than 3 ft. in diameter to more than ½ in. for columns exceeding 5 ft. in diameter. For very high-pressure columns or chambers the thickness is computed, and it may be as great as 4 in. for a column that is to operate at 1,000 lb. per square inch and at a high temperature.

Plate Design.—In the past columns containing only baffle plates were widely used, but such towers have been rapidly replaced by the more effective bubble-plate type of tower. However, the baffle-type tower is sometimes used for the following special services.

1. Fractionating very high-temperature vapor which tends to deposit coke.
2. Contacting hot vapor and cold oil for the purpose of pure heat-exchange or when the effectivensss of the separation or fractionation is not important.
3. For certain vacuum fractionation systems in which only an extremely small pressure-drop is permissible.
4. Fractionating materials that contain suspended matter, such as lime or coke.

Another type of column that is occasionally used is the packed column. However, packed columns should not be used in diameters exceeding about 20 in. because the liquid tends to channel and drain down the walls rather than through the packing. Packed columns are occasionally used as steam stripping columns if the quantity to be stripped is very small, but they are not used to a great extent in the oil industry.

Nearly all modern columns are modifications of the bubble-tower type of column. The vapor that travels up the column bubbles through a bath of reflux liquid that is contained on each plate. Figure 148 illustrates the general features of a bubble plate. The plates are most often constructed of plate steel. Steel plates are welded to the shell of the tower, but cast-iron trays must be sealed into the tower shell by means of packing. Cast iron is more resistant to corrosion than steel; but the major corrosive action takes place at the liquid-vapor contact line, and hence the superior resistance of the cast-iron plate is of little value. Cast-iron bubble caps are used almost exclusively, although pressed alloy-steel caps are sometimes used in vacuum-towers. Steel caps can be more closely spaced, thus allowing a larger area for the vapor as it passes through the caps. Many caps are of the removable type; *i.e.*, the vapor uptake and cap proper can be assembled on the plate. Usually a single bolt is used to fasten the cap, and the cap is sealed to the plate by a gasket. The fastening of caps to the plate by means of bolts is not an entirely satisfactory arrangement. The bolts become rusted, and many of the caps cannot be removed without breaking them. A more satisfactory arrangement is shown in Fig. 148. Here the vapor uptake-port is rolled into the plate, and the cap that sets over the uptake is held down by a bar. In other arrangements the heavy bell of the cap rests by its own weight

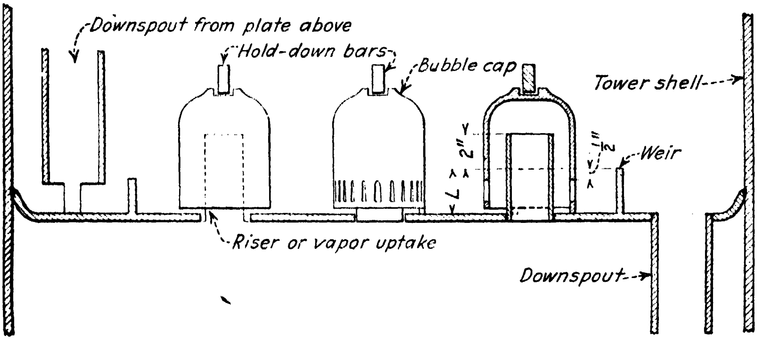

Fig. 148.—Features of a bubble plate.

over the uptake. Removable caps and a manhole above each plate are considered as best practice.

The exact design of the bubble cap is probably of little importance except from the standpoint of cost. The shape of the slots appears to have little or no effect.[2] The same shape of bubble is produced regardless of the shape of the slot. At low velocities[2] flat disk-shaped bubbles are produced; and at high velocities a channeling appears to occur, and a continuous elongated bubble space extends through the liquid. Contrary to common belief, Kallam[2] reports that more effective contacting occurs at low velocities than at high velocities.

Table 70 is a tabulation of the dimensions and areas of several bubble caps.

TABLE 70.—COMPARISON OF BUBBLE CAPS

Manufacturer	O.D., in.	Chimney or vapor uptake per cap, sq. ft.	Slots, area per cap, sq. ft.	$\frac{\text{Slot area}}{\text{Column area}}$	Material
A	4	0.0204	0.0372	0.144	C.I.
A	3	0.0232	0.0165	0.183	Steel
B	5	......	0.0356	0.115	C.I.
C	6½	......	0.0496	0.145	C.I.
D	4½	0.0204	0.0348	0.112	C.I.
E	4	0.0208	0.0396	0.150	C.I.
F	3 × 10*	0.1001	0.0921	0.161	C.I.

* Rectangular cap.

In addition to round or bell-shaped bubble caps, the so-called tunnel-type trays and caps are used by many companies. These trays consist of liquid troughs several feet in length, or even across the entire tray, and vapor uptakes of the same length. A curved elongated cap or tunnel lies over the uptake, causing the vapors to bubble through the trough of liquid. The trays function satisfactorily, although spouting of the liquid has been reported. Perhaps the difficulty was as much due to faulty leveling of the plates or placement of the tunnels as to errors in the theory of this type of plate.

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[2] KALLAM, F. L., Notes on Absorber Design No. 1, *Petroleum Eng.*, April, 1934, p. 33.

Many designs of the so-called sieve-type plates have been proposed from time to time, although they have never been adopted as standard tray designs. In these plates, small apertures are provided, and both the liquid and the vapor pass through the same opening. Obviously, such plates cannot be operated at a high capacity because the liquid fails to drain through the plate. However, these plates operate with very low pressure-drops, and hence they may become of importance in vacuum fractionation.

The design of the *downpipes* or *downspouts* which carry the overflow liquid from one tray to the next has not received the attention that it deserves. Many towers fail to perform properly simply because the downspouts are inadequate. The liquid that flows through the downpipe is in the form of a froth. The weir or edge of the downspout (Fig. 148) may be the limiting factor, or the cross-sectional area of the downpipe may cause liquid to accumulate. Either of these two factors will materially decrease the capacity of the fractionating tower.

Kallam[2] has made a study of the construction of downpipes. Several downspout arrangements were installed in the same tower. At an oil-to-gas ratio of 30 gal. of oil per thousand cubic feet of gas, the plates performed as shown in Table 71. A study of the fall-distance and the interference of several streams of oil flowing into the same downspout is also discussed.[2]

Table 71 indicates that two factors are involved in the performance of the downspout, one the area and the other the perimeter. However, the perimeter must be placed so that the liquid can overflow easily as well as be sufficiently long. The weir on plate 2 is effective along its entire length, but the weirs on the other plates are not completely effective.

At the present time the downspout periphery or perimeter is usually estimated by the weir formulae given in Chap. X, but an ample length of weir and an ample downspout area should be provided. The liquid velocity in the downpipe (based on no froth) usually should not exceed 4 in. per second. In many designs a velocity of 2 in. per second will not incur a large expense, and the use of a low velocity gives better results.

The overflow weir or dam is usually designed so that it will hold a liquid level (no froth) of 0.5 to 1.5 in. above the top of the slots. Actually, the liquid flows across the tray as a froth and the level equipment, must be kept at a minimum. In towers operating at atmospheric pressure, the average pressure-drop per plate is about as follows:

Top Tower Velocity, Ft. per Sec.	Lb. per Sq. In. per Plate
1	0.05
2	0.12
3	0.18
4	0.25

The pressure-drop increases as the amount of liquid that flows across the plate is increased. These figures are for normal rates of liquid flow. The pressure-drop through pressed-steel caps, when installed in vacuum-towers operating at about 40 mm. pressure, ranges from about 0.7 mm. per plate at a superficial vapor velocity of 7 ft. per second to about 1.2 mm. per plate at a velocity of 13 ft. per second. The submergence of the slots in the liquid was $\frac{1}{16}$ in.

Kallam[4] reports that absorption towers, operating at a superficial gas velocity of 1.1 ft. per second, give pressure-drops as follows:

Oil-to-gas ratio, gal. per 1,000 cu. ft.	Pressure-drop per plate, lb. per sq. in.	
	16 plate column	Single plate
10	0.04	0.02
30	0.06	0.08
50	0.08	0.14

As an aid in computing liquid quantities and the general conditions within the tower, the following data will prove useful. The properties of the various liquids in a tower approach a constant value if compared at the temperature in the tower. However, if a large amount of steam is used or if the processing is conducted in a vacuum, the constants are not exact. These data were compiled by using actual plant temperatures.

Specific gravity	0.684 (42.7 lb. per cu. ft.)
Surface tension	12.5 dynes per sq. cm.
Viscosity:	
Gas oil—470°F	0.45 centipoises
Kerosene—375°F	0.27 centipoises
Naphtha—335°F	0.23 centipoises

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[4] Notes on Absorber Design No. 2, *Petroleum Eng.*, June, 1934, p. 29.

Plate Spacing and Entrainment.—The obtainment of equilibrium on a bubble plate is governed by two opposing factors. One of these, the intimacy of vapor-liquid contact, tends to produce equilibrium; but if the contacting or bubbling is too violent, liquid particles will be carried from one plate to the next by the vapor and will tend to destroy the separation that has been obtained. Thus agitation produces equilibrium, but at the same time entrainment occurs and partly destroys the equilibrium.

Two kinds of entrainment can occur. One is a distinct splashing, spraying, or spouting of liquid particles. The particles are thrown upward by the velocity they attain at the slot of the cap, and they will fall back into the liquid if they expend their energy content before they reach the next plate. The liquid particles are relatively large, and a relatively high velocity is necessary to cause them to be thrown to a height of 18 in. This kind of entrainment can be eliminated almost entirely by placing the trays far apart.

The other kind of entrainment might be referred to as "carrying." Very small particles of liquid do not fall through the vapor as fast as the vapor rises, and they are carried by the vapor stream to the plate above. At a given velocity, all particles smaller than a certain size will be carried by the vapor to the plate above and the larger particles will fall slowly back to the parent plate. At ordinary vapor velocities, the size of the particle that can be carried from plate to plate by the vapor appears to be between 0.1 and 0.2 mm. in diameter.

Thus the velocity is limited by two factors: It should be high so that intimate contact will result, and yet it must not be so high that undue entrainment will occur. Chillas and Weir[5] report that entrainment is negligible at a velocity of 2 ft. per

Material	Pressure	Linear velocity, ft. per sec.	Per cent entrainment
Gasoline	Atmospheric	1.4	0.25
Gasoline	Atmospheric	3.0	0.8
Gas oil	20 mm.	10.0	1.8
Air-water	Atmospheric	0.3	0.04
Air-water	Atmospheric	2.2	0.7

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[5] *Ind. Eng. Chem.*, **22**, 206 (1930).

second but that it amounts to 7 and 20.5 per cent at 4 and 5.5 ft. per second. In commercial columns, having trays spaced at 22 in., the entrainment[6] is approximately as shown in the table on page 480.

Souders and Brown[7] have derived the theoretical suspending velocity, and they show the effect of tray spacing on entrainment. Equation (82) (page 485) for the allowable vapor velocity in columns is based on a consideration of entrainment. For a water-air system operating at the velocity normally maintained in petroleum towers, the entrainment at a spacing of 22 in. is less than 4 per cent of the entrainment at 12 in. In alcohol-water towers[3] the entrainment for a 1-in. seal (static) was found to be seven to eighteen times as great at a spacing of 12 in. as at 18 in., and actual entrainments were as follows:

Vapor velocity, ft. per sec.	Entrainment, mols liquid per mol dry gas		
	At 18-in. spacing	At 12-in. spacing	At 6-in. spacing
1.0	.....	.....	0.004
1.5	.....	0.006	0.25
2.5	.....	0.04	
3.0	0.006	0.11	
3.5	0.009	0.3	
5.0	0.033		
7.0	0.19		

The use of baffles or other devices to remove entrainment naturally permits the use of higher velocities. However, the cost of these devices and the difficulties with corrosion have been deterrents to their use. A separating device, termed the Centrifix,[8] appears to be effective in removing entrainment. This device has been used to clean the vapor from a tubestill before it enters the fractionating tower. Steel wool has been used for the same purpose, but it becomes plugged with coke and corrosion scale. When used in this manner, the Centrifix is effective in improving the color of the product that is withdrawn above the vaporizer and in reducing the amount of acid that is required to treat the product. The performance of the Centrifix separator is indicated in Table 72.[8] A 9-in. layer of steel wool[8] is able to reduce the color to about one-twentieth of the color when no wool is used. Chillas and Weir[9] have also studied the effect of a special baffle, similar to venetian blinds, on entrainment.

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[6] Analysis of commercial plates by the author.

[7] Fractionating Columns—Entrainment and Capacity, *Ref. Nat. Gaso. Mfr.*, January, 1934, p. 32.

[8] ANON., Prevention of Entrainment in Tube Still Processing, *Ref. Nat. Gaso. Mfr.*, February, 1934, p. 70.

TABLE 72.—REMOVAL OF ENTRAINMENT FROM VAPOR

Crude	Hivis product				
	Per cent of crude	Vis. at 210°	O.D.* color without Centrifix	O.D.* color with Centrifix	Color reduced to these per cents of original color
Reagan............	6	140	5,800	1,550	27.0
East Texas........	6	140	11,900	1,650	13.8
Little Panhandle...	5	125	13,400	4,000	30.0
Barbers Hill.......	8	145	3,600	1,500	42.0

* The optical density (O.D.) color scale of The Atlantic Refining Company is directly proportional to the depth of color.

Kallam[4] presents information concerning tray spacing. He finds that the capacity of an absorber was more than doubled by increasing the tray spacing from 7 to 14 in. and that at the same time half as many trays gave almost as good a separation. The trays in petroleum oil columns are usually spaced at 18 to 24 in., and for vacuum service they are sometimes spaced at 36 in. There are two reasons for this spacing: (1) The entrainment is low, and (2) space is available for the installation of manholes above each tray and for the steel bracing that is necessary in large-diameter towers. In several instances, refiners have found that the removal of every other tray in a closely spaced column (10 in.) has resulted in better fractionation. The spacing of the trays is involved in the velocity equation [Eq. (82), page 485]. By using Eq. (82), the cost of building and operating a crude oil topping tower is found to be lower at a spacing of about 25 in. than at any other spacing.

[9] *Ind. Eng. Chem.*, **22**, 206 (1930).

The centrifuge contactor[10] developed by Podbielniak promises radical improvements in our methods of conducting fractionation and other countercurrent processes. In a bubble-tower the separation of liquid and vapor between each plate is effected by means of gravity, whereas in the centrifuge contactor the separation is facilitated by means of centrifugal force. One arrangement of the equipment consists of a spiral plate having a space between turns of only ⅛ in. A connection for withdrawing the fractionated vapor and another for introducing reflux liquid are situated at the center of the spiral; and the mixture of vapor from the still is introduced at the outside of the spiral. The spiral revolves at a high speed and by centrifugal force causes the liquid to travel as a thin film along the entire length of the spiral plate from the center to the outside. The vapor travels in the opposite direction through the spiral, by the difference in pressure between the outside and the inside of the spiral. It is claimed that a vapor velocity of 40 to 80 ft. per second can be maintained because of the elimination of entrainment, and more than 50 theoretical plate equivalents can be obtained in a practical commercial equipment.

Plate Efficiency.—In general, plate efficiency is the ratio of the performance of an actual plate to the performance of some ideal plate. Plate efficiency may be defined as the ratio of the amount of a given component that is absorbed by the liquid upon the plate to the amount that would be absorbed were equilibrium actually attained.

A thermal definition has also been used. Plate efficiency may be defined as the heat actually removed from the vapor passing through the plate divided by the heat that would be removed if equilibrium were attained. At equilibrium the temperature of the vapor above a plate and of the liquid on the plate are equal, whereas on an actual plate the temperature of the vapor is higher than the temperature of the liquid.

The "ideal plate" tacitly assumed in fractionation equations is one in which all the vapor from the plate below comes in contact with liquid of constant composition from the plate above and is in equilibrium with the liquid overflowing to the plate below; *i.e.*, the ideal plate assumes a single perfect equilibrium contact per plate. However, plates in an actual column usually involve a number of successive contacts per plate. The liquid changes composition progressively as it flows across the plate, so that the vapor flowing through each successive row of caps approaches equilibrium with a liquid of different composition. Even if equilibrium were attained at each contact, the composition of the average vapor leaving the plate would be considerably different from the composition of the vapor that is in equilibrium with the liquid that overflows from the plate. It has been shown[11] that the successive contact plate, upon which equilibrium is attained at each contact, produces a greater change in the composition of the vapor passing through it (*i.e.*, it is more efficient under ideal conditions) than is the usual ideal plate which involves a single equilibrium contact. This phenomenon probably accounts for some of the high plate efficiencies (greater than 100 per cent) that have been reported in the literature.

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[10] Podbielniak Industrial Research and Engineering Laboratories, Chicago.

In general, plate efficiency may be regarded as the resultant of two distinct and opposing effects. One of these is the approach to equilibrium between liquid and vapor; the other, the entrainment of liquid by the vapor, tends to destroy the equilibrium that has been attained. Plate efficiency is an exceedingly complex factor. It varies with the mechanical details of plate and column, with vapor velocity and density, and with the properties of the oil. The plate efficiency differs not only for various fractionating towers but also from plate to plate in a single column.

The plate efficiency probably ranges from 70 to 90 per cent for petroleum oil columns. Authorities on natural-gasoline plant design use 55 to 65 per cent for absorber-column plates operating at a low pressure (30 to 50 lb. gage). The efficiency for high-pressure (400 to 600 lb.) absorber plates is said to be 45 to 55 per cent. However, Brown and others[12] report plate efficiencies of 100 to 108 per cent in the analysis of the performance of a commercial natural-gasoline stabilizer.

One of the most complete studies of plate efficiency has been made by Peavy and Baker,[3] but they studied alcohol-water. Their results indicate that entrainment is the main reason for

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[11] BREWSTER, O. C., *Oil Gas J.*, Apr. 3, 1930, p. 41.

[12] BROWN, SOUDERS, NYLAND, and HESLER, Design of Fractionating Columns, *Ref. Nat. Gaso. Mfr.*, May, 1935, p. 227.

Approx. vol....$459 \times 379 \times \frac{760}{30} \times \frac{490 + 460}{520}$ = 8,050,000 cu. ft. per hr.

Density of vapor.................................$\frac{119{,}400}{8{,}050{,}000} = 0.0148 = d_2$

Assume d_1 = 50 lb. per cu. ft. (it can be computed from Fig. 43).

$$d_2(d_1 - d_2) = 0.0148(50 - 0.0148) = 0.74$$

The constant C for a surface tension of 20 is about 700 (Fig. 150). The allowable mass velocity, W = 602.

$$\text{Cross-sectional area of tower} = \frac{119{,}400}{602} = 198 \text{ sq. ft.}$$

The diameter is 15.9 ft. with no factor of safety. (The actual tower that was used for these conditions was 17 ft. in diameter.) The linear velocity corresponding to the foregoing is 11.3 ft. per sec.

FRACTIONATION OF COMPLEX MIXTURES

The difficulties in outlining mathematically the process of fractionation as applied to complex mixtures have long been almost unsurmountable. The subject has been approached by numerous investigators,[15–26] but in all instances, including the method presented hereafter,[27] the methods are so complicated that application to specific design problems is impractical and may even be misleading owing to the accumulation of the effects of even small errors. In view of this situation, the most practical uses for these design methods are studies of the relations among such variables as amount of reflux, number of plates, and purity of products and as a means of establishing the fundamental con-

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[15] Brown and Souders, *Trans. Am. Inst. Chem. Eng.*, **30**, 438 (1934).

[16] Brown, Souders, and Hesler, *Trans. Am. Inst. Chem. Eng.*, **30**, 457 (1934).

[17] Brown, Souders, and Nyland, *Ind. Eng. Chem.*, **24**, 522 (1932).

[18] Fenske, M. R., *Ind. Eng. Chem.*, **24**, 482 (1932).

[19] Lewis and Wilde, *Trans. Am. Inst. Chem. Eng.*, **21**, 99 (1928).

[20] Lewis and Matheson, *Ind. Eng. Chem.*, **24**, 494 (1932).

[21] Lewis and Cope, *Ind. Eng. Chem.*, **24**, 498 (1932).

[22] Robinson and Gilliland, "The Elements of Fractional Distillation," McGraw-Hill Book Company, Inc., New York, 1939.

[23] Thiele and Geddes, *Ind. Eng. Chem.*, **24**, 289 (1933).

[24] Gilliland, E. R., *Ind. Eng. Chem.*, **27**, 260 (1935).

[25] Underwood, A. J. V., *J. Soc. Chem. Ind.*, **52**, 223T (1933); and *Trans. Inst. Chem. Eng.* (London), **10**, 112 (1932).

[26] Jenny, F. J., *Trans. Am. Inst. Chem. Eng.*, **35**, 635 (1939).

[27] Nelson and Roland, *Ind. Eng. Chem.*, **30**, 730 (1938); and ten articles in *Oil Gas J.* referred to later.

cepts and theory of fractionation. No simple methods are available, and they are so complicated and fraught with trial-and-error computations that investigators have found difficulty in even explaining their methods to others.

When applied to wide-boiling-range mixtures such as the customary refinery products (and natural gasoline) the following general facts become apparent.

1. Amount of *reflux* has little effect on the degree of fractionation or purity of products if normally large reflux ratios (4:1 in topping plants or 8:1 in stabilizers) are employed and if a normal number of plates (5 between cuts in topping plants or 20 in stabilizers) are used.[28,29] These amounts of reflux are almost equivalent in effect to infinite reflux, and hence the composition of the overhead product can be computed by the simple relationship shown in Eq. (83). The meaning of the symbols is given on page 493

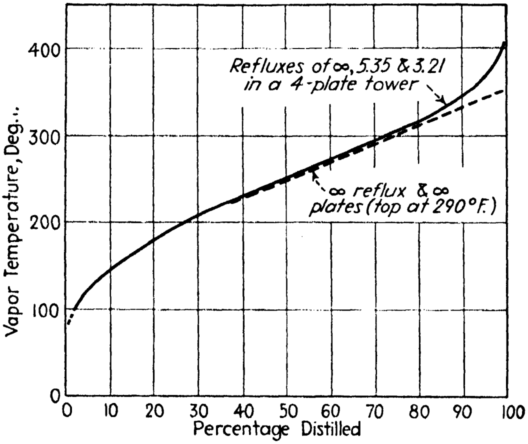

FIG. 151.—True boiling-point distillation curves of gasolines produced in a four plate using various quantities of reflux. Note also the curve for infinite reflux with infinite plates. (*Oil Gas J.*)

$$Y_1 = \frac{100C - wz}{g + \dfrac{hJ}{K_1K_2 \cdots K_n}}; \qquad \text{or} \qquad y_1 = \frac{100C - wz}{g + \dfrac{h}{K_1K_2 \cdots K_n}} \tag{83}$$

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[28] NELSON, W. L., Effect of Reflux on Fractionation, *Oil Gas J.*, Aug. 18, 1938, p. 58.

[29] NELSON, W. L., Natural Gaso. Stabilizer Fractionation-plant Data, *Oil Gas J.*, Oct. 20, 1938, p. 59.

As illustrations, the computed compositions of overhead products by Eq. (83) are compared in the following tabulation with the actual plant[29] product, and Fig. 151[30] indicates the distillation curves of products from a topping plant operating with different amounts of reflux. The check on plant operation is not perfect, but the relationship is so complicated if infinite reflux is not assumed that the method is scarcely practical (page 496).

Component	Percentage of components		
	Actual	Using true reflux	Assuming ∞ reflux
CH_4	2.58	2.56	2.58
C_2H_6	13.35	13.34	13.68
C_3H_8	78.20	78.46	79.20
iC_4H_{10}	5.27	5.45	4.40
C_4H_{10}	0.35	0.19	0.14
iC_5H_{12}	0.25*	trace	trace

* Analysis in error.

2. *Yields* in topping plants are not affected more than ± 1.5 per cent, based on feed-stock, by the degree of fractionation that is attained, provided usual amounts of reflux and numbers of plates are employed. This is illustrated by the yields of 385 E.P. gasoline shown in the following tabulation:[30]

EFFECT OF REFLUX ON GASOLINE YIELD FROM A 4-PLATE TOWER

Reflux ratio	99% point of product*	Yields, per cent		Notes
		Gasoline	Kerosene	
∞	401	28.7	21.3	Infinite reflux
5.35	400	27.9	22.1	Usual reflux
3.21	400	27.6	22.4	Least reflux
1.07	415	....	....	Insufficient reflux

* About 15°F. higher than the A.S.T.M. end-point (Fig. 81).

3. *Number of plates* has a vital effect on the end-point of the product, but at 4 or more plates (topping plant) the difference in

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[30] NELSON, W. L., Effect of Fractionation on Yield, *Oil Gas J.*, Oct. 6, 1938, p. 56.

end-point is only about 10°F. if normal reflux ratios are employed. More than 10 plates (topping plants) have little effect on the degree of fractionation.[31] Although Fig. 152 indicates that the end-point is scarcely different for 2 plates than for 6 plates, it should be borne in mind that the high end-point when using 2 plates cannot be reduced even by using infinite reflux and hence the only recourse would be to reduce the yield of gasoline drastically in order to get a lower end-point.

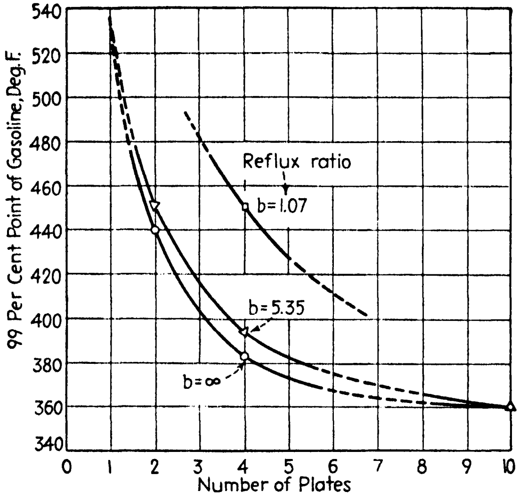

FIG. 152.—Relation of number of plates to 99 per cent point (top plate at 290°F.). (*Oil Gas J.*)

In gasoline stabilizers the situation is not clear. Ten plates fail to separate propane from the gasoline or recover all isopentane, even at infinite reflux, but the use of more than 40 plates does not appear to be justified for any operation.[32]

4. *Plate efficiency* appears always to exceed 75 per cent and is often close to 100 per cent.[27] It is suggested that an efficiency of 80 per cent is a reasonably safe design value.

5. The selection of *plate temperatures* is the most unsatisfactory part of the design method. Intermediate plate temperatures are not of vital significance, but the temperatures at the plates

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[31] NELSON, W. L., Effect of Varying Number of Plates, *Oil Gas J.*, Sept. 15, 1938, p. 46.

[32] NELSON, W. L., General Application and Summary, *Oil Gas J.*, Dec. 15, 1938, p. 46.

at which products are withdrawn or feeds are admitted must be computed with great care.[32]

Theory of Fractionation.—The complicated behavior of complex mixtures requires the use of many symbols and several new concepts (see Fig. 153).

R = mols internal (or hot) reflux at top, based on a heat-balance and including no reflux for the plates below the first side-draw plate.
eR = mols actual reflux as a fraction of R, includes excess reflux that flows from the base of the column to other plates that lie below the first side-draw plate.
n = plate number, counting from top.
a = total number of plates between two products being separated.
D = mols overhead product.
b = reflux ratio $= eR/D$.
O = mols overflow liquid or reflux at any point.
V = mols vapor at any point.
x = mol percentage of fraction being considered, liquids.
y = mols percentage of fraction being considered, vapors.
P = vapor-pressure of fraction.
π = total pressure (abs.) of system, same units as P.
$K = y/x = P/\pi$ = equilibrium constant.
m = molecular weight of fraction.
m_p = molecular weight of overhead or top product.
m_{n+1} = molecular weight of bottom product ($n + 1$ plate) of tower section studied.
d = density of fraction.
d_p = density of overhead product.
d_{n+1} = density of ($n + 1$) material.
y_1 = mol percentage of fraction in overhead product.
Y_1 = liquid-volume-percentage of fraction in overhead product.
y_{n+1} = mol percentage of fraction in bottom product of tower section studied.
Y_{n+1} = liquid-volume-percentage of fraction in bottom product of tower section studied.
J = a constant by which the ratio of mol percentages is multiplied to convert the ratio to a basis of liquid-volume-percentage.

$J = m_p d_{n+1}/m_{n+1} d_p$.
C = liquid-volume-percentage of fraction in feed-stock.
g = percentage of top product based on feed-stock.
h = percentage of bottom product based on feed-stock.
wz = product of percentage and composition of fractions that leave a multiproduct tower system in other products than the two that are being studied.

Each pair of two products with the plates between them is considered as a separate fractionating tower or section and will be so handled throughout this entire discussion. Reflux in a complex-mixture column decreases from plate to plate by an amount equal to R divided by a, as indicated in Fig. 153. Thus, the reflux consists of two parts; a quantity R, which disappears entirely in the column, and an excess reflux related to e, which flows through the column in undiminished amount, and may be considered as reflux for the sections or fractionating columns that are below the one being studied. The reflux at any or the nth plate is

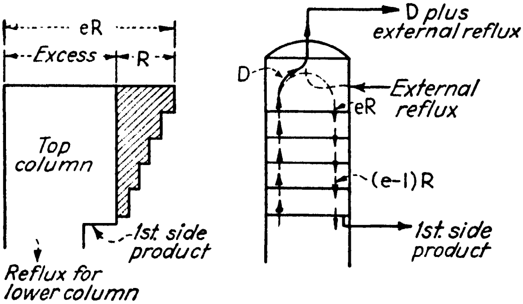

FIG. 153.—Reflux conditions in the top section of a multiple-product fractionating tower.

$$O_n = eR - \frac{R}{a}n = bD\left(1 - \frac{n}{ea}\right) \tag{84}$$

Other relationships and a derivation of the final equations that will be presented later may be found in original references,[33,34,27-32] but they are too long to be presented here.

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[33] NELSON, W. L., *Oil Gas J.*, July 21, 1938, p. 41; Aug. 4, 1938, p. 44; Oct. 27, 1938, p. 178; and Nov. 10, 1938, p. 44.

[34] NELSON, W. L., Intermediate Towers, *Oil Gas J.*, Dec. 1, 1938, p. 40.

If the tower products are liquids, mol percentage is converted to a liquid percentage basis by means of the constant J and equilibrium constants. Thus, for relating vapor concentrations at the top and bottom of a tower section, the relation is

$$\frac{y_{n+1}}{y_1}(J) = \frac{Y_{n+1}}{Y_1} \tag{85}$$

whereas for relating a vapor at the top to the liquid flowing from the base of the tower section

$$\frac{y_{n+1}}{y_1}\left(\frac{J}{K_{n+1}}\right) = \frac{x_{n+1}}{y_1}(J) = \frac{X_{n+1}}{Y_1} \tag{86}$$

Or for an intermediate tower section in which both the top and bottom products are withdrawn as liquids (as in separating kerosene from gas oil in a topping tower), the relation is

$$\frac{y_{n+1}}{y_1}\left(\frac{K_1}{K_{n+1}} J\right) = \frac{x_{n+1}}{x_1}(J) = \frac{X_{n+1}}{X_1} \tag{87}$$

The composition of the feed is related to the composition of the products by a material balance. For a tower section producing a vapor product at the top and a liquid product at the bottom:

$$100C = gY_1 + hX_{n+1} + w_1z_1 + w_2z_2 + \cdots \tag{88}$$

The sum of the w_1z_1, w_2z_2, etc., terms are all combined in Eq. (89) as wz.

or

$$Y_1 = \frac{100C - wz}{\dfrac{hJ}{K_{n+1}}\left(\dfrac{y_{n+1}}{y_1}\right) + g} \tag{89}$$

The mol percentage ratio (y_{n+1}/y_1) shown below the line is related to reflux, number of plates, temperature, and pressure (equilibrium constants) as indicated in Eqs. (90), (91), (92), (93), and (94) (page 496), which could have been written as a general but very complicated form. Rather than confuse the presentation, it appeared best to let the reader devise additional equations by inspection of those given and not present a confusing general equation.

Two-plate tower:

$$Y_1 = \frac{100C - wz}{g + \dfrac{hJ}{K_2R\left(\dfrac{D}{R} + e - 1\right)}\left[D + \dfrac{R(e-1)}{K_1}\right]} \tag{90}$$

Three-plate tower:

$$Y_1 = \frac{100C - wz}{g + \dfrac{2hJ}{K_3R\left(2\dfrac{D}{R} + 2e - 1\right)^2}\left[D\left(2\dfrac{D}{R} + 2e - 1\right) + \dfrac{D}{K}(2e-2) + \dfrac{R(2e-2)^2}{2K_1K_2}\right]} \tag{91}$$

Four-plate tower:

$$Y_1 = \frac{100C - wz}{g + \dfrac{3hJ}{K_4R\left(3\dfrac{D}{R} + 3e - 1\right)^3}\left[D\left(3\dfrac{D}{R} + 3e - 1\right)^2 + \dfrac{D}{K_3}(3e-3)\left(3\dfrac{D}{R} + 3e - 1\right) + \dfrac{D}{K_2K_3}(3e-3)^2 + \dfrac{R(3e-3)^3}{3K_1K_2K_3}\right]} \tag{92}$$

Five-plate tower:

$$Y_1 = \frac{100C - wz}{g + \dfrac{4hJ}{K_5R\left(4\dfrac{D}{R} + 4e - 1\right)^4}\left[D\left(4\dfrac{D}{R} + 4e - 1\right)^3 + \dfrac{D}{K_4}(4e-4)\left(4\dfrac{D}{R} + 4e - 1\right)^2 + \dfrac{D}{K_3K_4}(4e-4)^2\left(4\dfrac{D}{R} + 4e - 1\right) + \dfrac{D}{K_2K_3K_4}(4e-4)^3 + \dfrac{R(4e-4)^4}{4K_1K_2K_3K_4}\right]} \tag{93}$$

Six-plate tower:

$$Y_1 = \frac{100C - wz}{g + \dfrac{5hJ}{K_6R\left(5\dfrac{D}{R} + 5e - 1\right)^5}\left[D\left(5\dfrac{D}{R} + 5e - 1\right)^4 + \dfrac{D(5e-5)}{K_5}\left(5\dfrac{D}{R} + 5e - 1\right)^3 + \dfrac{D(5e-5)^2}{K_4K_5}\left(5\dfrac{D}{R} + 5e - 1\right)^2 + \dfrac{D(5e-5)^3}{K_3K_4K_5}\left(5\dfrac{D}{R} + 5e - 1\right) + \dfrac{D(5e-5)^4}{K_2K_3K_4K_5} + \dfrac{R(5e-5)^5}{5K_1K_2K_3K_4K_5}\right]} \tag{94}$$

Intermediate towers, which are defined as those from which both bottom and top products are withdrawn as liquids, are indicated in Fig. 154. The study of such towers is complicated by the fact that the reflux (X_R) does not have the same composition as the overhead (liquid) product and in fact is intermediate in composition between Y_1 and X_1. Perhaps the best approach is to use the equations that have already been given and that assume that $X_R = Y_1$, because these equations are more simple than others; but as an illustration of the relationship if X_R is assumed to be equal to X_1, Eq. (95) for a three-plate tower is presented. Note that Eq. (91) is far more complicated than Eq. (95), which is also for a three-plate tower. Additional relations for two- and four-plate towers are given in the original references.[34]

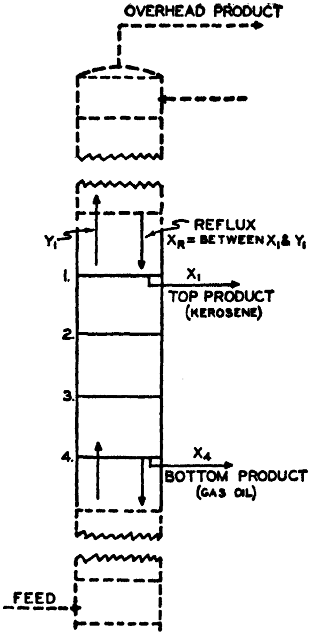

Fig. 154.—Diagram of intermediate tower system of four plates. (*Oil Gas J.*)

Three-plate tower:

$$X_1 = \frac{100C - wz}{g + hJ\frac{K_1}{K_2}\left[\frac{\frac{D}{R} + e}{\frac{D}{R} + e - 1} - \frac{1}{K_1}\frac{e}{\frac{D}{R} + e - 1} + \frac{1}{K_2}\frac{e\left(2\frac{D}{R} - \frac{2R}{eD} + 1\right)}{\left(\frac{D}{R} + e - 1\right)\left(2\frac{D}{R} + 2e - 1\right)} + \frac{1}{K_1K_2}\frac{(2e - 3)}{\left(2\frac{D}{R} + 2e - 2\right)\left(2\frac{D}{R} + 2e - 1\right)}\right]} \quad (95)$$

All the preceding equations are very complicated, and hence in many instances the use of Eq. (83) for infinite reflux may be justified

$$Y_1 = \frac{100C - wz}{g + \dfrac{hJ}{K_1K_2 \cdot \cdot \cdot K_n}} \tag{83}$$

The use of this equation gives nearly the same results as the more complicated equations if the reflux quantity is as large as that normally used commercially and if a normal number of trays is employed. Another powerful reason for using Eq. (83) is the fact that equilibrium constants (K's) are not dependable when applied to complex mixtures and hence great expenditure of energy in using the more rigorous equations may not be justified. The infinite reflux equation [Eq. (83)] should not be used for those intermediate towers which lie just above the feed plate, because such towers operate with very little reflux.

In two-component fractionation studies (pages 264–270) the term minimum reflux is employed as the amount of reflux below which no increase in the number of plates (even to infinity) will cause the separation of the desired product. Although such a situation also exists for complex mixtures, in that a particular boiling-range of product cannot be produced unless a certain amount of reflux is employed, the situation of minimum reflux is not clear for practical purposes because the composition of the overhead product cannot be easily defined. Thus, if the spread in temperature between the 90 and 99 per cent point is fixed, a certain minimum reflux is necessary; whereas if another difference in temperature between the 90 and 99 per cent points is permitted, another minimum reflux will be required. One situation, however, is completely clear; *i.e.*, the *least reflux* that can be employed must always be more than for a value of $e = 1$. This means that in all situations the actual reflux eR must be greater than the reflux R that is demanded by a heat balance. At lower quantities of reflux, no liquid would overflow from the base of the column into lower intermediate columns, and hence any material that once found its way into the column as a vapor would of necessity be found in the two products from the column because no other outlet exists. In many instances the intermediate section of column situated just above the feed plate of a multiple-draw column operates with just slightly more reflux than that required by least reflux.

Application of Fractionation Equations.—In applying the fractionation equations a number of factors prove to be confusing. Fractionation computations are based primarily on the mols of the various products undergoing separation and their vapor-pressures, and hence a true-boiling-point distillation curve of the feed must be available. The distillation curves obtained by the computation are also true-boiling-point curves. Exact correlations of true-boiling-point versus A.S.T.M. curves are not available, particularly for the low-boiling end of the distillations, but a correlation dependable as far as it goes is given in Fig. 81. This figure may be used to estimate the A.S.T.M. curves of the products.

Yields must be estimated as a preliminary step in the computations. These can be determined by the general methods outlined in Chap. VII, but it should be recalled that maximum yields cannot be obtained (perfect fractionation) unless an infinite number of trays and infinite reflux are employed. Thus, the plant yields will be slightly different from those determined in Chap. VII—a lower yield of top product and different yields of intermediate products because of the overlap of the products. The accuracy of the estimated yields will be checked and corrected by trial-and-error methods during the fractionation computations.

After the yields are determined, the temperatures in the tower must be computed or estimated by the methods outlined in the early parts of this chapter and the general theory outlined in Chap. XIV. In heavy-oil towers the temperatures on the plates that lie between the plates from which products are withdrawn can be estimated with relative ease and accuracy, but in gasoline stabilizers and other operations requiring a large number of plates the estimation of accurate plate temperatures is difficult. In general, the plate temperature changes most rapidly at or near the plates from which products are being withdrawn. The feed plate does not molest the temperature gradient greatly unless the feed is introduced at the wrong point in the column—and this situation is almost unavoidable in most multiple-draw columns. In general, the smaller the amount of reflux the greater the change in temperature at or near the withdrawal plates.

Some plant data on the temperature gradients in gasoline stabilizers are available.[35]

In most instances it is necessary to assume that vapor-pressure is a suitable measure of equilibrium relations, since experimental equilibrium constants are not available for the heavy hydrocarbons or complex mixtures. More is known of the equilibrium constants of the low-boiling hydrocarbons but not so much as would be useful. The vapor-pressures given in Fig. 52 and the constants in Figs. 70–74 and Tables 33 and 34 may be used. These data were used in checking several plant operations[27,29] and were found to give accurate results for a plate efficiency of 80 to 100 per cent. The questionable accuracy of the equilibrium constants that are available makes it necessary to look upon the fractionation equations as a method of studying the relation of variables such as amount of reflux and number of plates rather than as a means of designing specific fractionation systems. This means that for most purposes the somewhat simple equation for infinite reflux [Eq. (83)] may be used rather than the more complicated equations.

Example 74. Fractionation of Gasoline and Kerosene.—The crude oil shown in Fig. 103 is to be fractionated into gasoline, kerosene, and other products. The top five plates of the tower, which separate gasoline from kerosene, operate at an equivalent pressure of 1,000 mm. including the partial-pressure reduction of steam. The gasoline is to have an end-point of about 380°F., and the kerosene is to have a gravity of 46 A.P.I.

By perfect fractionation the yield of gasoline would be about 30.5 per cent and the yield of kerosene about 20 per cent. However, as a result of losses and the overlap by imperfect fractionation, the true yields will be assumed to be as follows:

Gasoline	26.0 per cent 62 A.P.I.
Kerosene	23.5 per cent 46 A.P.I.
Total	49.5 per cent

These assumed yields will be checked in the computations that follow; and should they be found to be incorrect, it will be necessary to make new assumptions and repeat all of the computations.

The five actual plates will behave as about four theoretically perfect plates if the plate efficiency is assumed to be 80 per cent. In order to facilitate the computations, the infinite reflux equation [Eq. (83)] will be employed, but at the end of the example, the manner of using Eq. (92), which applies to any amount of reflux, will be indicated.

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[35] Burdick, *Oil Gas J.*, Apr. 9, 1931, p. 26; Brown, Souders, Nyland, and Hesler, *Ref. Nat. Gaso. Mfr.*, May, 1935, p. 227; Lewis and Smoley, Studies in Distillation, *Proc. A.P.I.*, *Div. Refining*, 1929; Ragatz and McFadden, *Oil Gas J.*, May 13, 1937, p. 68; and Wells, *Oil Gas J.*, June 11, 1931, p. 22.

$$Y_1 = \frac{100C - wz}{g + \dfrac{hJ}{K_1K_2K_3K_4}} \tag{83}$$

The yield of gasoline is g, or 26, and of kerosene is h, or 23.5. The value of J must be computed by recourse to Fig. 35 and densities

$$J = \frac{m_p d_4}{m_4 d_p} = \frac{115 \times 0.797}{193 \times 0.731} = 0.648$$

If we are interested only in getting the composition of the gasoline and of the front end of the kerosene, the wz term (or terms) can be neglected because essentially none of the hydrocarbons in the gasoline and low kerosene will be lost into heavier products such as gas oil. By inserting known values, the equation simplifies to

$$Y_1 = \frac{100C - 0}{26 + \dfrac{23.5 \times 0.648}{K_1K_2K_3K_4}} = \frac{100C}{26 + \dfrac{15.2}{K_1K_2K_3K_4}}$$

The remaining variables, *i.e.*, the equilibrium constants (K's) and C, are dependent upon the composition of the feed and the plate temperatures. Values of C are determined by reading from Fig. 103 (p. 358) and are smoothed by inspection as shown in column (3) of Table 75. The values of K, as shown in columns (5), (6), (7), and (8) of Table 75, can be read from Figs. 5 or 52, but it is first necessary to estimate the plate temperatures. By means of the approximate boiling-ranges of the products taken from Fig. 103 and the methods outlined on pages 467–473 of this chapter, the plate temperatures are found to be about as follows:

	Plate No.	Deg. F.
Gasoline	Top plate	310
	2	360
	3	400
Kerosene	4	425

In Table 75, column (12) should total to 100 per cent if the assumed yields of gasoline and kerosene designated as g and h, respectively, are correct. The total of column (12) was 100.52; and had new values of $g = 26.2$ and $h = 23.3$ been used, the total would have been almost exactly 100. The error so introduced occurs primarily in the first two fractions, and hence the error of 0.52 per cent was corrected in column (13) in the first two numbers, *i.e.*, 27.3 and 35.3.

One other check on the accuracy must be made before the computations can be dismissed as correct. This check consists in determining the tower temperatures from the computed distillation curves shown in columns (13)

TABLE 75.—TABULATED COMPUTATIONS FOR EXAMPLE 74

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)
Fraction No.	Boiling range	C	$100C$	Vapor pressures divided by 1,000 at				$K_1K_2K_3K_4$	$\frac{15.2}{(9)}$	(10)+26	$Y_1 = \frac{100C}{(11)}$	Gasoline, percentage	$\frac{gY_1}{26\times(12)}$	$100C - gY_1$ (4) − (14)	X_{n+1} (15) ÷ 23.5	Kerosene, percentage
				310°F.	360°F.	400°F.	425°F.									
1	80–200	7.2	720	6.50	11.00	16.0	19.0	21,800	0.0007	26.0	27.70	27.3	720	0	0	
2	200–220	2.1	210	3.00	5.30	8.2	10.5	1,370	0.0111	26.01	8.08	35.3	.....	.....	0	
3	220–240	2.15	215	2.40	4.20	6.4	8.0	516	0.0294	26.03	8.35	43.6	.....	.....	0	
4	240–260	2.2	220	1.80	3.20	4.9	6.5	183	0.0830	26.08	8.44	52.1	219.4	0.6	0.02	
5	260–270	1.22	122	1.45	2.65	4.1	5.4	85	0.179	26.18	4.66	56.7	121	1	0.04	
6	270–280	1.22	122	1.35	2.40	3.8	4.9	60.4	0.252	26.25	4.65	61.4	121	1	0.04	0.1
7	280–290	1.22	122	1.10	2.10	3.3	4.2	32.0	0.475	26.47	4.61	66.0	120	2	0.09	0.2
8	290–300	1.22	122	0.98	1.85	3.0	3.8	20.7	0.735	26.73	4.57	70.5	119	3	0.13	0.3
9	300–310	1.22	122	0.83	1.60	2.7	3.3	11.8	1.29	27.29	4.48	75.0	116	6	0.26	0.6
10	310–320	1.22	122	0.72	1.40	2.3	3.1	7.18	2.12	28.12	4.35	79.4	113	9	0.38	1.0
11	320–330	1.22	122	0.62	1.24	2.1	2.7	4.35	3.49	29.49	4.14	83.5	107.5	14.5	0.62	1.6
12	330–340	1.22	122	0.54	1.08	1.85	2.4	2.58	5.89	31.89	3.82	87.3	99.4	22.6	0.96	2.5
13	340–350	1.22	122	0.47	0.97	1.6	2.2	1.61	9.44	35.44	3.46	90.8	90.0	32.0	1.36	3.9
14	350–360	1.22	122	0.40	0.83	1.4	1.95	0.905	16.8	42.80	2.85	93.6	74.1	47.8	2.03	5.9
15	360–370	1.22	122	0.345	0.71	1.22	1.70	0.508	30.0	56.0	2.18	95.8	56.6	65.4	2.78	8.7
16	370–380	1.22	122	0.295	0.62	1.1	1.54	0.312	48.7	74.7	1.63	97.4	42.4	79.6	3.39	12.1
17	380–390	1.22	122	0.250	0.54	0.96	1.30	0.168	90.5	116.5	1.05	98.5	27.3	94.7	4.03	16.1
18	390–400	1.22	122	0.210	0.47	0.82	1.13	0.0915	166.0	192.	0.64	99.1	16.6	105.4	4.49	20.6
19	400–410	1.22	122	0.162	0.41	0.73	1.01	0.0490	310.0	336.	0.36	99.5	9.4	112.6	4.79	25.4
20	410–420	1.22	122	0.140	0.36	0.64	0.90	0.0290	524.0	550.	0.22	99.7	5.7	116.3	4.85	30.3
21	420–440	2.44	244	0.118	0.28	0.52	0.74	0.0127	1200.0	1226.	0.20	99.9	5.2	238.8	10.18	40.4
22	440–460	2.44	244	0.086	0.21	0.40	0.57	0.00412	3700.0	3726.	0.06	.....	1.6	242.4	10.32	50.8
23	460–480	2.44	244	0.058	0.15	0.29	0.425	0.00107	14200.0	14226.	0.02	100.0	0.5	243.5	10.37	61.1
24	480–500	2.44	244	.....	.....	.....	.....	....	....	large	0.00	.....	0.0	244.0	10.38	71.5
										Total = 100.52						

Explanation of column headings:
(1) Number assigned for identification.
(3) Percentage of fraction in feed-stock.
(5) to (8) Equilibrium constants taken at mean boiling-point of fraction except big fractions such as No. 1.
(10) $hJ/K_1K_2K_3K_4$.
(11) Denominator of Eq. (83).
(12) Equation (83).
(13) Cumulative percentage of fractions.
(14) Starting material balance, Eq. (88).
(15) Part of Eq. (88).
(16) Equation (88).
(17) Cumulative percentage.

and (17) of Table 75 and on Fig. 155. The checks on the assumption of 310 and 425°F. were found to be satisfactory. A.S.T.M. curves estimated by means of Fig. 81 are also shown in Fig. 155.

Equation for Actual Reflux.—Had Eq. (92) been used, it would have been necessary to make a heat-balance such as that illustrated in Example 33 (page 198). According to such a heat balance (using 100 gal. as a basis), the actual hot reflux or eR = 6.6 mols.

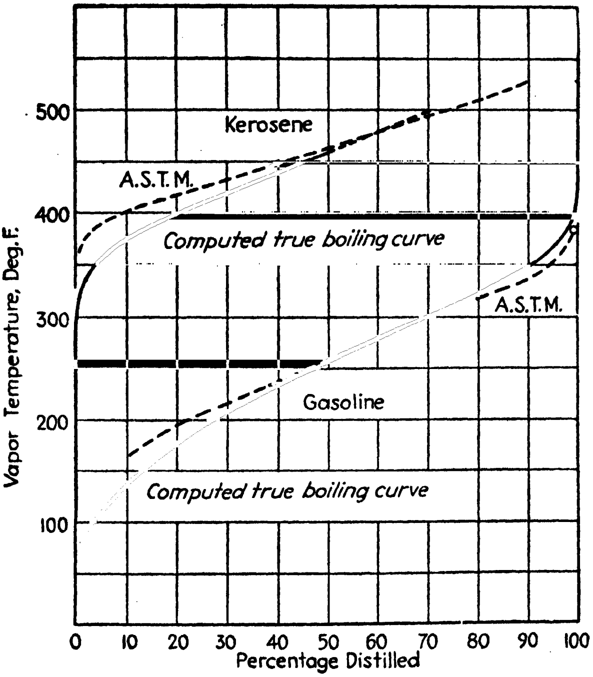

FIG. 155.—Composition of products determined in Example 74.

The heat-balance reflux R for the top five plates is (191 lb. of gasoline)

$$\text{Reflux heat} = 191(425 - 310)0.52 = 11{,}400 \text{ B.t.u. per hr.}$$

$$R = \frac{11{,}400}{121 \times 113} = 0.833 \text{ mol}$$

$$e = \frac{6.6}{0.833} = 7.93$$

$$D = {}^{191}\!/_{113} = 1.69$$

$$b = \frac{eR}{D} = \frac{6.6}{1.69} = 3.9$$

$$\frac{D}{R} = \frac{1.69}{0.833} = 2.03$$

$$J = 0.648$$

By inserting these values in Eq. (92) the following simplified equation results:

$$Y_1 = \frac{100C}{g + h\left(\frac{0.1365}{K_4} + \frac{0.098}{K_3K_4} + \frac{0.0701}{K_2K_3K_4} + \frac{0.241}{K_1K_2K_3K_4}\right)}$$

The computations are conducted in the same manner as for infinite reflux. Note, however, that the top temperature will be slightly lower and that the yields will be slightly different.

Plant Practice.—Although design computations such as those described on previous pages are useful for outlining fractionation theory, the design of fractionating columns is usually conducted by rule-of-thumb methods. The separation of most refinery products is such an easy separation that four or five equilibrium contacts are usually sufficient. As an approximation, the number of trays (at 22-in. spacing) that are now being used between fractions is indicated in Table 76.

TABLE 76.—NUMBER OF TRAYS USED IN COMMERCIAL EQUIPMENT

Operation	Materials	Plates between fractions
Steam, atmospheric	Gasoline and kerosene	5–6
	Gasoline and naphtha	4–5
	Naphtha and kerosene	4–5
	Kerosene and gas oil	4–5
	Gas oil and wax distillate	3–5
	Stripping plates	4–5
	Gas oil and vaporizer	2–3
Cracking	Pressure distillate and recycle	7–9
Brightstock solution	Naphtha and gas oil	4–5
	Gas oil and neutral	5–6
	Neutral and feed plate	3–5
	Stripping plates	4–5
Lubricating oil	Gas oil and wax distillate,* vacuum	2–3†
	Wax distillate and overhead cylinder stock, atmospheric	7–10
	Wax distillate and overhead cylinder stock, vacuum	3–4†

* Often separated by partial condensation.

† At wide tray spacing (30 in.).

Fractionation is more effective at low pressures than at high pressures because of the larger difference in the vapor-pressures of the components at a low pressure. This probably accounts for the relatively few plates that are used in many vacuum plants, although the wide tray spacing that is normally used accounts in part for the lesser number of trays.

As indicated earlier in the chapter, fractionation is disturbed in the multiple-draw column because the lower boiling products pass the plates in the column from which the high-boiling products are withdrawn. Thus side-draw products are bound to contain low-boiling materials, and no amount of fractionation can completely eliminate this difficulty. These light components are customarily removed from the side-draw products by the use of auxiliary steam stripping columns. Each of the side-draw products is allowed to flow through about four bubble plates in the steam stripping column. Although the stripping column usually appears to be about as tall as the main fractionating column, in

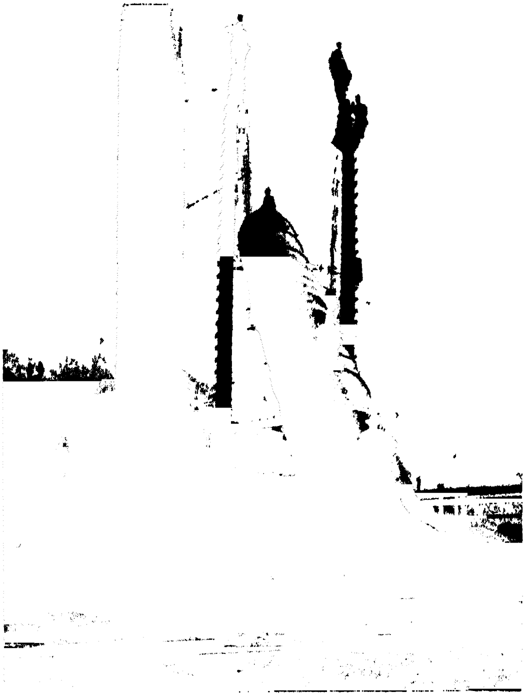

FIG. 156.—Erecting a bubble-tower. (*A. J. Smith Engineering Company.*)

reality it consists of separate distinct columns, one above another, and a separate stripper is used for each side-draw product. Steam is admitted to each stripping column, and the vapor (steam and a small amount of light material) from each stripper is allowed to pass back into the main column at the tray above the side-draw plate. Thus the steam stripper governs the initial boiling-point or flash-point of the product, but the degree of fractionation obtained in the main column governs the end-point.

The use of internal stripping sections is becoming more and more common. The stripping tower is smaller than the main tower, and hence it can be built within the main tower.

Steam strippers are designed in the same manner as fractionating columns. In determining the diameter, the volume of the steam is all that is usually considered.

References

(Earlier references appear in the First Edition of this book)

BROWN and HOLCOMB: Vapor-liquid Phase Equilibria in Hydrocarbon Systems, Part VII, (calculating minimum plates), *Petroleum Eng.*, July, 1940, p. 31.

GILLILAND, E. R.: Multicomponent Rectification, *Ind. Eng. Chem.*, **32**, 1220 (1940).

CHAPTER XXIV

CRACKING AND OTHER CHEMICAL PROCESSES

Although the commercial practice of cracking functions by the principles outlined in Chap. XVII, it has not been guided to a large extent by these principles. As is so often the case in industrial development, commercial improvements have preceded the development of engineering theory. Perhaps the greatest hindrance to rapid commercial development has been difficulties in the fabrication of materials that could withstand the high temperatures and pressures necessary in most cracking processes. Even today several processes await commercial development because they require cheap and dependable materials for working at 1000 to 1200°F. or pressures of 3,000 to 10,000 lb. per square inch.

Although a large number of commercial processes, such as the Burton, Fleming, Jenkins, Cross, Dubbs, and Holmes Manley, have been used during 1910–1940, the patents covering these processes have been consolidated to a large extent, with the result that the general processing scheme outlined in this chapter has been adopted by most refiners. The yields are nearly the same from all types of plants; the products have much the same properties; and the operating efficiency is nearly uniform. For a detailed discussion of early cracking processes and patents, refer to "Motor Fuels" by E. H. Leslie,[1] "American Petroleum Refining" by Bell,[2] and the first edition (1936) of this book.

The commercial development of catalytic cracking processes and other chemical processes has taken place even more recently. By these means, the raw oil stocks may be converted into types of hydrocarbons that are not present in the original charge-stocks. Among the processes are the Houdry catalytic process, several catalytic and thermal polymerization processes, and thermal and catalytic alkylation processes. These will be discussed in later parts of this chapter. They open the door what may be called a petroleum chemical industry (see Cha. XVIII).

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[1] Leslie, E. H., "Motor Fuels," Chemical Catalog Company, Inc., New York, 1923.

[2] Bell, H. S., "American Petroleum Refining," 2d ed., D. Van Nostrand Company, Inc., New York, 1930.

Most of the new processes are now being employed for the manufacture of gasoline, but to an increasing extent the raw stocks produced from these processes will be utilized for the manufacture of chemical materials rather than gasoline. The gasoline produced by these processes is universally high in octane number, and as blending-stock it behaves as if it had even higher octane numbers. The new processes will not completely displace the older ones of gasoline manufacture, *viz.*, crude oil topping and cracking. Rather they are being used as auxiliaries to our regular processes. Evidence of this development is clear in such arrangements as combination cracking plants (Fig. 162) and in such combination processes as cracking (or reforming) and catalytic polymerization; cracking and Houdry catalytic cracking; and natural-gasoline stabilization and polymerization. More and more the several new processes are being used as chains of processing operations for the manufacture of specific hydrocarbons. An example is the so-called isooctane processes, which involve the following general steps:

1. Dehydrogenation to produce olefin hydrocarbons.
2. Catalytic polymerization.
3. Complete sulfur removal.
4. Hydrogenation to produce a saturated product.
5. Parts 2, 3 and 4 replaced by catalytic alkylation of olefins and isoparaffins.

THERMAL CRACKING

Modern cracking processes are expected to produce a large yield of gasoline, produce little coke, and be able to operate for a long period of time before cleaning is necessary. The formation of coke is necessarily related to the length of operation, because the unit must be shut down to remove the coke. The percentage of time that the unit is in active operation is referred to as the cycle-time-efficiency. For example, if the unit can operate for 45 days and then requires 5 days for shut-down, cleaning, repair, and time to get onstream, the cycle efficiency is 90 per cent. The expense of shut-down time is so great that it is usually more economical to sacrifice some yield than to have a poor cycle efficiency. This accounts, in part, for the relatively small amount of coking that is practiced. The yield by cracking is much greater if coke, rather than fuel oil, is produced, but the cost of operating a coking plant is great.

Cracking processes may be generally classified as follows:

1. *Viscosity Breaking.*—A short-time decomposition, usually conducted at low cracking temperatures (830 to 870°F.), for the purpose of reducing the viscosity or pour-point of a heavy straight-run fuel oil.
2. *Mixed-phase Cracking.*—Most of the widely known processes are classed as mixed-phase processes. The name liquid-phase, which is often used, is a misnomer, because in most processes some vapor generation occurs. The purpose is the production of antiknock gasoline and a greater total yield of gasoline from crude oil.
3. *Reforming.*—A cracking process that utilizes a straight-run gasoline or naphtha as a charging-stock. The cracked distillate has a much higher octane number than the charging-stock. The feasibility of the process depends upon the market demand for high-octane fuel. A high temperature must be employed.
4. *Selective Cracking.*—A process in which the charge-stock is separated into several parts, each part being cracked separately under the most favorable conditions for that part. Thus, the plant might utilize four cracking coils: one for viscosity breaking, another for reforming, and two other coils to handle light and heavy charge-stocks.
5. *Combination Cracking.*—A process involving the four processes enumerated above and one that in the extreme might also involve topping of crude oil, gas recovery, and even coking.
6. *Vapor-phase Cracking.*—These processes are usually more expensive than the liquid-phase processes, but the gasoline is highly antiknock and can be sold at a premium as a blending stock.
7. *Coking.*—The operation of coking involves nothing more than a cracking process in which the time of cracking is so long that coke is produced as the bottoms product. Special means of collecting and removing the coke must be provided.

Cracking Plant Design.—The major difference between liquid- or mixed-phase and vapor-phase cracking is the pressure that is used. In the liquid-phase and mixed-phase processes, the pressure is usually held above 350 lb. per square inch. This pressure is above the critical pressure of most hydrocarbons that are found in cracking-stocks (and products), and hence a very dense phase, whether it be liquid or a mixture of liquid and vapor, is produced. The density of the vapor, if any is formed, is high, and hence little or no stratification of the mixture occurs at the velocities that are maintained in the cracking-tubes of the pipestill. A lower pressure may result in a separation of liquid and vapor, and the liquid that adheres to the walls may be decomposed into coke. There are other differences between liquid- and vapor-phase processes such as the type of stocks that may be cracked and the temperature-pressure-relation. The liquid- and mixed-phase operations are characterized by the use of a relatively low temperature and high pressure, whereas the vapor-phase operations are characterized by a relatively high temperature and a low pressure.

In vapor-phase processes, the pressure is normally less than 100 lb. per square inch (often 35 lb.) and a pure vapor-phase is produced. The time in the cracking-tubes is short because of the great volume of material, and hence the temperature must be higher than for liquid- or mixed-phase operation. The importance of a *homogeneous phase* must again be stressed. If any liquid particles are present in the vapor, they will be thrown to the tube walls and cause the formation of coke.

The time of cracking in modern processes ranges from about 1 sec. for some vapor-phase processes to about 200 sec. for liquid-phase processes. Such short times as these must be carefully controlled, and hence most modern processes are arranged so that the hot cracked material can be suddenly cooled by means of the charge-stock or fuel oil from the process. This operation is referred to as *quenching*.

Another factor that is vital in the operation of many cracking systems is the production and cracking of only *clean distilled stocks*. If a residual product is to be cracked, the gas oil that it contains is distilled from it in a topping operation; this topping may be conducted in the cracking plant itself, or the system may be arranged so that only straight-run tar is cracked. The cycle efficiency is usually much higher if only distilled stocks are cracked. Unless a cracking-pipestill is carefully designed, coke will be deposited in the tubes and will cause a shut-down after about a week if a residual stock is passed through the tubes. Even coking processes depend upon a clean stock for heating the coke chamber (Fig. 161).

Although the cracking of a distilled stock is advantageous from the standpoint of the cycle-time-efficiency, the yield of pressure distillate is usually slightly smaller than when a *residual* or *black stock* is cracked. If a distilled stock is produced from a black charging-stock, a part of the charging-stock is not thoroughly cracked, and therefore the yield is smaller. Likewise, the tar that is produced by cracking only the distilled part of a black charging-stock tends to have a high viscosity, and the yield of distillate must be less in order to produce a tar of suitable viscosity. If the difficulties of heating and cracking a black stock in the cracking-tubes can be solved, the cracking of the entire black stock in the tubes is advantageous. The Dubbs process was one of the first processes that was able to avoid serious coking of the tubes when cracking a black stock.

If a black stock is cracked in the tubes, it is always advantageous to separate the cracked tar produced in the cracking reaction and allow none of it to enter the cracking-tubes during recycling.

The conversion-per-pass used in cracking plants and related decomposition processes is a function of the material being cracked and the cracking temperature. The higher the temperature the lower the allowable conversion-per-pass, and the lower boiling the stock the greater the allowable conversion-per-pass. Furthermore, the higher the carbon content of the stock (tars or recycle stocks) the lower the allowable conversion-per-pass. Thus, in commercial units, the following conversions[3] are used:

	Per Cent
Viscosity breaking.................	3–10 (usually once through)
Light virgin and refractory stocks...	14–30 (high values for once through)
Heavy virgin and refractory stocks..	10–18 (recycling)

The use of a quench-stock, the production of a homogeneous phase, the use of recycling, and the cracking of stocks that contain no cracked tar are details that are not easily recognized in flow diagrams of processes, but close inspection reveals that almost all successful processes utilize these principles.

The velocity (hot) of the oil-vapor mixture in the cracking-tubes must exceed about 15 ft. per second, or coke will be deposited. Most processes maintain a velocity of 20 to 40 ft. per second (hot). Higher velocities would be advantageous except that the pressure-drop becomes prohibitive. Thus if a pressure of 450 lb. is to be held at the outlet of the still, the charging pressure, at a velocity of 40 ft. per second, will be about 850 lb. per square inch. As coking takes place, the charge-pressure rises to over 1,000 lb. per square inch. The rate of heat absorp-

[3] Smoley, Mekler, and Schutte, Combination Selective Cracking, *Ref. Nat. Gaso. Mfr.*, June, 1937, p. 288.

tion in the pipestill usually ranges from 10,000 to 14,000 B.t.u. per square foot of projected area (3200 to 4500 B.t.u. per square foot outside-diameter surface). These low rates can be produced in the radiant section by using a large amount of radiant surface, by using flue-gas recirculation, or by using large amounts of excess air. Part of the convection section may be used for the cracking zone, but the exact location in the convection section cannot be easily determined. Some engineers believe that cracking must take place at a constant or slightly rising temperature, or coke will be deposited.

Selective Cracking.—In Chap. XVII it was indicated that each stock has particular characteristics that govern the best conditions of temperature, pressure, etc., for cracking the stock. Advantage of this fact is utilized in selective combination cracking units in which the refractory stocks are cracked for a long period of time or at a higher temperature and the less stable stocks are cracked at lower temperatures. Thus, for a four-coil (or heater) unit operating on Mid-Continent stocks, temperatures and pressures[3] are about as follows:

	Temperature, deg. F.	Outlet pressure, lb. per sq. in.
Viscosity breaking heater	870– 890	230–250
Heavy oil heater	920– 960	300–500
Light oil heater	950– 990	500–700
Reforming heater (once through)	975–1000	650–800

Larger yields are obtained in this manner, and for very large plants the use of selective cracking is always justified. In smaller plants the erection of several pipestills is costly, or the operation of several coils in one furnace is difficult, and hence the position of selective cracking is not clear. Separate evaporators may be used for each stock, but common practice is to use a single evaporator into which all stocks are led.

In wide-boiling-range stocks the refractory low-boiling parts are insufficiently cracked at low temperatures, with the result that they accumulate in the recycle stock—or at high temperatures the high-boiling parts are cracked so violently that coke formation takes place.

Technical details of design computations and theoretical aspects were discussed more fully in Chap. XVII entitled Thermal Decomposition.

Volume of Stock at Decomposition-temperature.—The computation of volumes at extreme temperatures and pressures is always troublesome and at the best can only be looked upon as an estimate. An illustration of such computations is given on page 323, Example 59. The theory underlying the phase relationships of complex mixtures is discussed on page 247, Chap. XIV. The extremely high density of the vapors that are present under high pressures should not be overlooked. In no sense are these vapors comparable to what we normally conceive to be gases.

Fundamentals of Processing.—There is a striking similarity between all of the widely used modern cracking processes. Many processes crack only a clean distilled stock, and the hot stock from the pipestill tubes is quickly cooled by a quench-stock. Other processes have reaction chambers or soaking drums by which the capacity and yield are increased, but drums and chambers are not necessary unless coke is to be produced. The arrangement of the equipment, *i.e.*, stills, towers, evaporators, etc., is different for the several processes, but the fundamentals of the processing are much the same in all of them.

Following the establishment or discovery of these fundamentals, the development of modern cracking processes may be directly traced to the development of suitable construction materials. Lyman C. Huff[4] says,

> Among these are large forged-steel and electric-welded vessels, such as reaction chambers and dephlegmators, heavy seamless-steel tubing in iron-pipe sizes, alloy steel tubing, welded pipe joints, metal-to-metal high-pressure flange joints, alloy-steel studs and bolts, alloy-steel forgings and castings, high-temperature and high-pressure cast and forged-steel valves and fittings, high-temperature and high-pressure pumps (handling oil up to 800°F. and 1,500 lb. pressure), fans for circulating flue gases at high temperatures (1100 to 1200°F.), high-temperature insulating materials and many others.

Of almost equal importance was the formulation of the theories of heating and the application of these theories in the plant, so that mild absorption rates could be maintained in the pipestill.

[4] *Oil Gas J.*, Oct. 9, 1930, p. 138.

Obviously, the modern cracking processes could not have been developed without developing the pipestill.

Only four general types of cracking equipment will be discussed. These will be the so-called tubestill process which will be utilized in illustrating the fundamentals of plant operation, the Gyro vapor-phase process for illustrating cracking in the vapor-phase, coking processes for illustrating the handling of solid deposits, and a combination process for illustrating the practice of crude oil topping, viscosity breaking, reforming, and other related processes at the same time and in one plant.

Tubestill Processes.—Nearly all processes, particularly the Donnelly, the Winkler-Koch, and the Dubbs, discovered at much the same time the possibilities of conducting cracking in the tubes of a pipestill, and hence the general process so evolved is referred to as the tubestill process. Practically all of the cracking takes place within the furnace tubes so that no reaction chambers are required. The success of the process is largely due to the production of a clean cracking-stock which can be cracked with the production of little or no coke. A small amount of decomposition also takes place in the evaporator (Fig. 157) or flash drum, but this decomposition is not important, except as it aids in reducing the viscosity of the pressure-still tar and in producing additional clean recycle stock. The vapor heat exchangers shown in Fig. 157 are a source of difficulty, and the use of an additional pipestill heater is a better arrangement.

In order to crack the oil in the short length of time during which it passes through the tubes, a high temperature is necessary. The pipestill outlet temperature is about 890 to 940°F. depending on the stock, and the time for cracking is only 2 or 3 min. At these rapid rates of cracking it is necessary to lower the temperature quickly. This is accomplished at the point marked "quench" in Fig. 157 by mixing the charging-stock with the cracked material from the pressure-still. Mixing in this manner is a perfect means of heat-exchange, and hence the maximum amount of heat contained in the pressure-still product is recovered and utilized in vaporizing the charging-stock.

Continuous operation for periods of 3 months is common, although the operation is occasionally terminated by the formation of coke within the tubes. In maintaining long cycles of operation, the condition of the charge to the furnace is of prime importance. If this stock contains any tar by imperfect separation in the fractionating tower, coking proceeds immediately, and after 6 hr. of operation on a dirty charge-stock the tubes will often be badly coked and the operation must be halted. A low conversion-per-pass is necessary in avoiding coke formation. A conversion of 15 to 18 per cent is adequate for clean distilled stocks, but only 11 to 14 per cent can be used with clean but undistilled (black) stocks. Thus, if reduced crude oil is charged to the cracking furnace, a larger recycle ratio must be used.

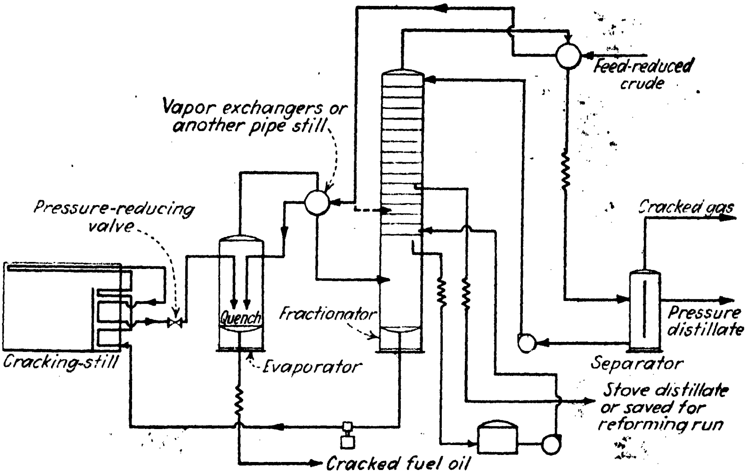

FIG. 157.—Simplified flow diagram of the tubestill cracking process.

Although many of these plants operate on a gas oil charging-stock, it is becoming more and more common to charge a reduced crude stock as shown in Fig. 157. Thus the topping of gas oil from reduced crude oil is accomplished within the cracking plant itself, but only the gas oil is exposed to cracking conditions. The viscosity of the tar, when charging gas oil, is relatively low, but it may be too high for market specifications if reduced crude oil is the charging-stock. This difficulty may be remedied by lowering the evaporator temperature and producing less gasoline. A vaporizer temperature higher than 820°F. will usually cause the deposition of coke in the evaporator.

The cracking-tubes may be in the convection or radiant section, but in either case the rate of heat input should be kept below about 13,000 B.t.u. per square foot of projected area per hour.

Furthermore, the hot velocity should be maintained at 20 ft. per second or higher. An outlet pressure of 400 to 700 lb. per square inch is maintained at the outlet of the pipestill. Lower pressures result in the formation of coke; and though we know little of the phase condition at such temperatures and pressures, it is conceded that a large generation of vapor takes place even at a pressure of 700 lb. per square inch. A pressure-drop of 300 to 800 lb. per square inch occurs through the pressure-still, so that inlet pressures of 700 to 1,200 lb. per square inch are common. Twin-simplex, compound steam cylinder pumps or crank-and-flywheel steam-engine pumps are commonly used (Fig. 158). Multistage centrifugal pumps are being used more and more widely (Fig. 159).

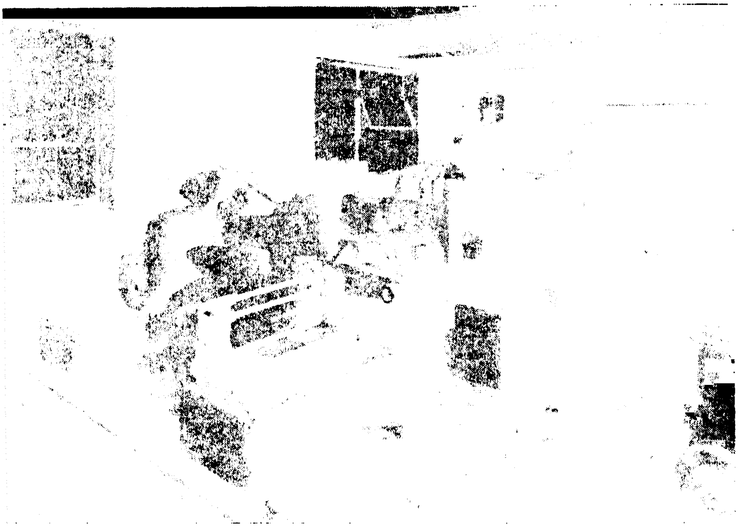

Fig. 158.—Installing a Wilson Snyder twin-simplex compound pump for high temperatures and pressures. (*A. J. Smith Engineering Company.*)

This process has been used for vapor-phase cracking without changing the fundamentals of the process. However, the outlet temperature is much higher (1050 to 1100°), and the outlet pressure must be reduced to 30 to 50 lb. per square inch so that substantially a pure vapor-phase exists in the cracking-tubes. Milder rates of heating and higher recycle ratios must be used. Difficulty arises because cracking starts to occur before vaporization is complete and coke is deposited in some section of the still.

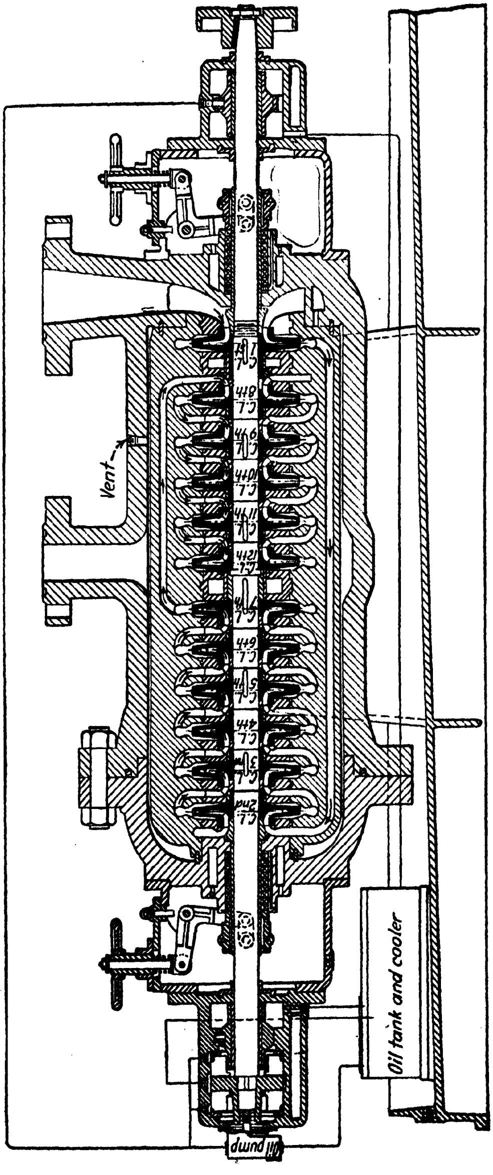

FIG. 159.—Twelve-stage hot oil centrifugal pump for oil at temperature of 850°F. and a pressure of 1,500 lb. per sq. in. (*Byron Jackson Pump Company.*)

The best known continuous coking processes are like this process except that coke drums are substituted for the evaporator vessel of the tubestill process (Fig. 161).

In processing topped or reduced crude oil, the maximum yield of gasoline is largely dependent upon the properties of the pressure-still tar. If too high an evaporator or vaporizer temperature is used or if the time in the evaporator is too short, the tar may be a solid asphaltic material, which is awkward to handle and cannot be marketed. In processing gas oil, this difficulty seldom arises because the tar consists almost entirely of cracked tar which has a lower viscosity. However, an evaporator temperature of about 820°F. cannot be exceeded because coke will be deposited in the evaporator. The large yield of 56.5 per cent of end-point gasoline shown in the third operation of Table 77 indicates the increased yields that are possible with a high evaporator temperature. In this operation, approximately 80 per cent of the topped crude oil was vaporized. However, this

TABLE 77.—YIELDS AND OPERATING CONDITIONS FOR SIMPLE CRACKING UNITS

Charge-stock	A.P.I.	Per cent 437 E.P. gasoline	Per cent tar and P.D. butts	Lb. coke per bbl.	Evaporator temp., deg. F.	Pressure at outlet	Cycle efficiency*	Notes
1. M.C. topped crude	23.9	49.5	47.8	......	780	750	.....	Cracking temp., 901°F.
2. M.C. topped crude	23.9	38.0	60.8	......	730	700	....	Cracking temp., 915°F.
3. M.C. topped crude	23.9	56.5	41.7	......	807	400	Low	
4. Calif. gas oil	18.5	51.0	42.0					
5. {38% M.C. topped crude 62% M.C. gas oil	20.2 28.3	49.8	48.7	......	758	400		
6. West Tex. fuel oil	21.8	60.55	12.6	56	...	185	0.80	Coking operation
7. Pa. gas oil	37.8	72.8†	9.2	29.7	...	267	0.89	Coking operation
8. M.C. topped crude	24.0	44.4‡	53.53	......	...	153	0.86	Flashing operation
9. Calif. gas oil	32.1	61.8	28.2	.009	...	300	0.88	Flashing operation
10. West Tex. residue	21.4	37.1	61.2	.026	...	180	0.88	Low-level operation

* Assuming 12-hr. shut-down for coking operation and 48-hr. for other operations.

† 425°F. end-point.

‡ 428°F end-point.

operation was not entirely successful because coking occurred within two weeks and the tar had a Furol viscosity of over 1,200 sec. at 122°F. In processing reduced crude oil, it is sometimes necessary to use a second pipestill for heating the reduced crude oil. The evaporator temperature may not be high enough with the vapor heat exchangers alone.

Yields and operating conditions by several mixed-phase (or liquid-phase) processes are given in Table 77. More definite yield information may be had by Eqs. (48) to (51), Chap. XVII.

Vapor-phase Processes.—The Gyro process was one of the first processes successfully to overcome the difficulties of cracking in the vapor-phase. Major among these difficulties had been the formation of coke, the short length of the operating period, and difficulties in treating the distillate. At the same time, a large amount of gas was produced, and until recently the yield of gasoline by vapor-phase processes was relatively low. With the widespread use of gasoline-recovery and polymerization plants, the total yield is now nearly equal to those of mixed-phase processes. In the Gyro process, the formation of coke is now largely avoided by the production of a pure dry vapor.

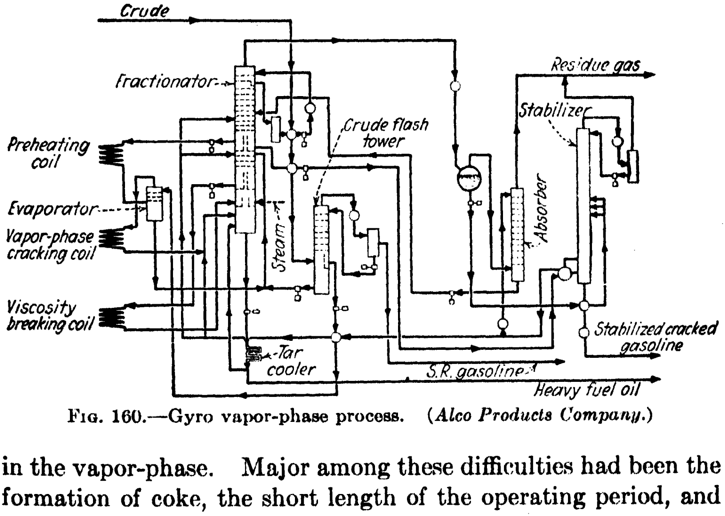

FIG. 160.—Gyro vapor-phase process. (*Alco Products Company.*)

At present the Gyro process compares favorably with the common liquid-phase processes in cost of operation, length of cycle, and yields. Figure 160 indicates that any charging-stock may be used and that the equipment is simple and flexible. However, only the gas oil distilled from the charge-stock is cracked. The finished gasoline often has an octane number of 85 or more, which is in general higher than the octane number of the gasoline produced by other processes. The gas is of a highly unsaturated nature and is of great importance as a raw stock for the manufacture of chemicals. An important mechanical advantage is the relatively low pressure that is used. The pressure at the evaporator is 10 to 40 lb. per square inch,[5] and at the pipestill outlet the pressure is about the same and only great enough to force the product through the fractionating and condensing system.

Common operating temperatures are still-outlet temperature, 1150°F.; oil from economizer, 700°F.; and temperature at evaporator, 600°F. The cycle efficiency of the Gyro process is reported to be over 96 per cent when operated with normal stocks.

Table 78 shows yield data for the Gyro and de Florez processes. A relatively large amount of gas is produced in vapor-phase processes, and hence gasoline absorption and stabilizer systems must be employed (Fig. 160).

TABLE 78.—YIELDS BY VAPOR-PHASE PROCESSES

Charging-stock	A.P.I.	Gasoline, per cent	Tar, per cent	Gas, per cent	Process	Reference and notes
Still bottoms.....	15	40.9	45.3	10.9	Gyro	7
Topped crude....	27	57.0	30.9	11.9	Gyro	7
Gas oil..........	30–34	75.1	11.4	12.5	Gyro	7
Pa. gas oil.......	.....	63.8	14.1	26.8	Gyro	7
Pa. gas oil.......	.....	61.4*	7.9	29.2	deFlorez	6

* Probably yield of untreated distillate.

The true vapor-phase process[8] involves the recycling of the gaseous products of cracking through the cracking coil to effect a maximum yield of gasoline by cracking, polymerization, alkylation, etc.

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[5] WAGNER, C. R., Vapor-phase Cracking, *Petroleum Eng.*, November, 1929.

[6] DEFLOREZ, L., A New Type of Cracking Unit, 10th Ann. Meeting A.P.I., Chicago, December, 1929.

[7] *Ref. Nat. Gaso. Mfr.*, February, 1932, p. 116.

[8] PRAEGER, F., *Ref. Nat. Gaso. Mfr.*, May, 1938, p. 207.

Coking.—The production of coke is accomplished by lengthening the time of cracking. The equipment used in modern semi-continuous processes is much the same as that used in cracking processes except that drums, chambers, or reaction vessels must be provided for the accumulation of the coke. Several coke drums are usually provided so that several of them can be emptied while another is onstream. At least three coke drums are necessary because time is required to dry the coke and difficulties frequently arise in the removal of the coke.

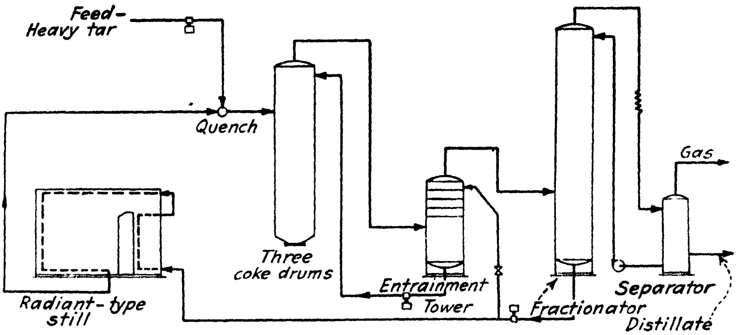

FIG. 161.—Semi-continuous coking system.

Semi-continuous cokers were not successful for many years because the black tarry stock was exposed to cracking conditions in the tubestill. Most of the processes that are now successfully operating are of the general type shown in Fig. 161. A clean distilled stock is produced from the coke drum, along with gas and distillate, and this distilled stock is recycled through the furnace and the coke drum and back to the fractionating system. The small entrainment tower is provided to ensure that no black material gets into the furnace charge-stock. The temperature in the coke drum is sustained entirely by the recirculating stream. Much of the cracking occurs in the pipestill tubes, but the drum is necessary to prolong the time and for the accumulation of coke.

Again it will be noted that the process is similar to the tubestill process shown in Fig. 157. It differs from the latter in that coke drums replace the evaporator of the tubestill process. The entrainment tower would probably be an advantage in the tubestill process. Normally no heat-exchange is used because the cold charge-stock is usually viscous and the exchangers tend to become plugged.

In the earlier cracking processes, notably the Dubbs process, a reaction chamber or chambers were provided so that the plant could be operated as a coking plant. Coke has been removed by means of a special steel cable which is suspended in spiral form from the top to the bottom of the chamber. At the end of the run the cable is pulled through the bottom manhole, cutting through the coke and breaking it so that it may be dropped through the bottom manhole. Large drills are also used to cut the coke from the reaction chamber, and in some instances high-pressure water nozzles[9] are used.

Knowles coking ovens involve increased flexibility in operation and produce a uniform high-quality coke.[10] A cracked fuel oil, which has been flashed down to a gravity of 1 to 2 A.P.I. is introduced slowly into the oven for about 100 min. or until a 10-in. layer of coke is produced. The coke bed is dried by heating for about 3 hr., reaching a final temperature of 1200°F., and is then removed by opening doors at both ends of the oven and ramming the hot coke into a quench-car by means of a large mechanical ram.

Almost pure carbon or artificial graphite, which is suitable for carbon electrodes, motor brushes, dry cells, etc., can be made by calcining petroleum coke.[11] In this process, the refinery coke is passed through a 100- to 125-ft. cylindrical rotating kiln by which it is heated to a bright red heat.

Combination Cracking Units.—The large amount of heat that can be recovered from a cracking plant, the advantages of cracking selected stocks at optimum operating conditions, and the general similarity of such operations as cracking, viscosity breaking, and reforming have led to the development of processes that comprise a combination of operations. Among the operations that have been advantageously combined are to be found the following:

1. Crude oil topping, using a separate tower for straight-run distillates.
2. Viscosity breaking, usually a once-through operation on straight-run residuum, although admission of black stock to the cracking coil is practical in some plants.

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[9] Court, W. F., Hydraulic Decoking of Coke Chambers, *Proc. A.P.I. Refining Div.*, Chicago, 1938.

[10] Foster, A. L., Lubrite Converts Fuel Oil into More Profitable Products, *Nat. Petroleum News*, May 6, 1936, p. 33.

[11] Stockman, L. P., First California Calcining Unit . . . , *Oil Gas J.*, July 4, 1940, p. 36.

3. Reforming of naphtha, usually as a once-through operation but also as a recycling operation—and sometimes employing a catalyst.
4. Selective cracking of several boiling-ranges of stock.
5. Coking of cracked tar.
6. Vacuum flashing of hot cracked tar for asphalt or to produce more recycle stock.
7. Gasoline recovery from the cracked gas.
8. Polymerization of olefin gases and decomposition of saturated gases.
9. Stabilization of gasolines and pressure distillate.

Operations 2, 3 and 4 are so similar in principle that they can be centered about a single evaporator or vaporizer. In each of these processes the cracked stocks must be currently freed from cracked tar if coking of the tubes is to be avoided. Thus in Fig. 162 all these stocks are led to a common evaporator vessel, and the commingled vaporized parts proceed to a single fractionating tower. In this tower the several recycle stocks are separated from one another and sent back to their respective cracking coils. If coking is practiced, the evaporator would be replaced by coking chambers and an entrainment vessel much as shown in Fig. 161. Operations 7 and 8, *viz.*, gasoline recovery and polymerization, are also similar in principle, and hence the recovery of any gaseous products, either natural or polymer, may be conducted in a common absorption and stabilizing system.

Figure 162 has purposely been simplified to permit illustration of the principles that are involved—and it should not be considered as a working flow diagram. In commercial practice many elaborations have been used or found necessary. As illustrations, several evaporator vessels and fractionating towers may be used rather than a single vessel; the polymerization processing may be conducted in a separate evaporator, fractionator, and absorption system; or a pipestill may be used instead of heat exchangers. In many instances the complicated processing utilized in actual plants is due to the use of old equipment that by itself is not large enough to handle the combined stocks indicated in Fig. 162. For more detailed information refer to the current literature.[3,12,13,14,15]

[12] WILLIAMS, N., Atlantic Refinery on Gulf Coast, *Oil Gas J.*, Feb. 23, 1939, p. 70.

[13] EGLOFF and NELSON, Modern Cracking Process, *Oil Gas J.*, June 25, 1936, p. 50.

[14] ANON., New Richfield Refinery, *Oil Gas J.*, Mar. 2, 1939, p. 36.

[15] SMOLEY, E. R., Combination Cracking Economics, *Ref. Nat. Gaso. Mfr.*, May, 1938, p. 184.

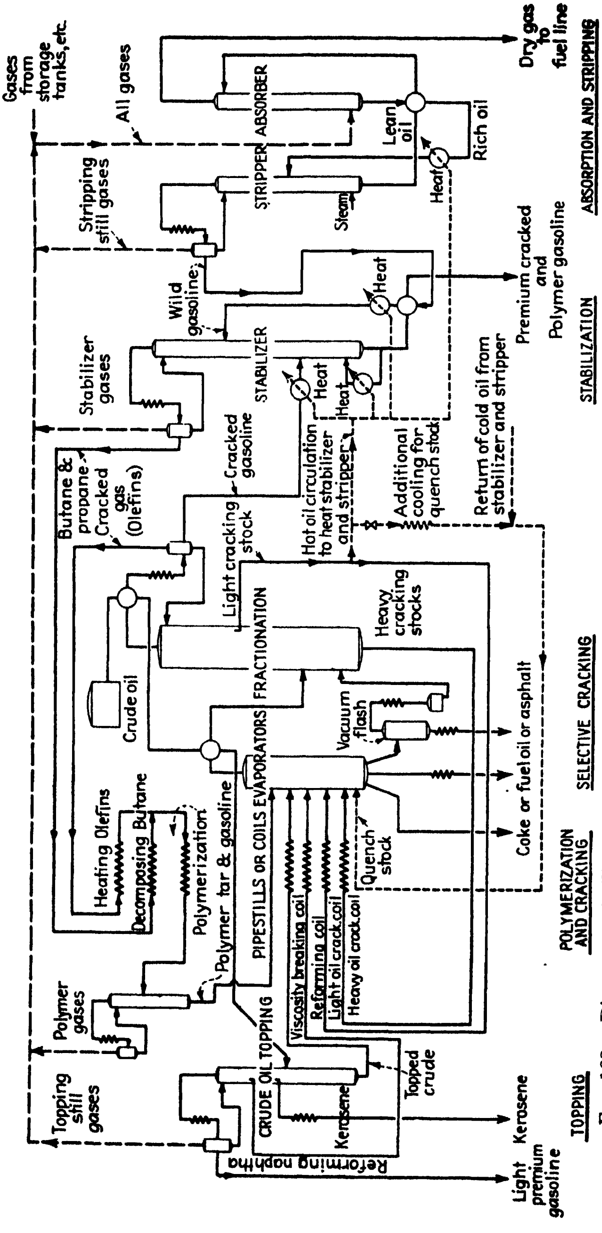

FIG. 162.—Diagrammatic illustration of the many operations that may be used in a combination cracking unit.

Yields by combination processes are, of course, a summation of the yields from the separate operations. An indication of yields is given in Table 79.

TABLE 79.—YIELDS BY COMBINATION CRACKING PROCESSES

	East Texas crude 39 A.P.I.	East Texas crude 38.6 A.P.I.	East Texas crude		M.C. crude 36.9 A.P.I.	Michigan crude 39.9 A.P.I.	M.C. crude 36.9 A.P.I.		
Straight-run gasoline	19.7	....	18.5	18.5	26.8	7.3	33	26	20
Cracked gasoline	43.7	....	39.3	39.3	41.5	56.9	36	42	45
Poly gasoline	none	....	5.2	....	none	none	none	none	none
Total gasoline	63.4	70.6	63.0	57.8	68.3	64.2	69	68	65
Furnace distillate	....	....	12.0						
Fuel oil	28.9	18.6	20.0	....	25.2	25.1	25.0	25.0	25.0
Gas and loss	7.7	10.6	5.0	10.2	6.5	10.7	6.0	7.0	10.0
Fuel oil, A.P.I	12.4	4.3	....	....	9.2	9.6			
Gasoline (total), octane No.	69.2	68.0	70.0	....	66.0	63.0	63.0	66.0	70.0
Reference	13	13	12	12	3	3	15	15	15

Viscosity breaking is conducted for the purpose of decreasing the viscosity or pour-point of an otherwise unsalable residue. The oil is heated to 830 to 890°F., and a yield of 5 to 15 per cent pressure distillate is produced. The results of several bomb cracking tests are shown in Table 80.[16] A similar operation, which consists of heating a heavy residue to 870 to 900°F. for the purpose of distilling additional gas oil cracking-stock, is practiced by some refiners. Decomposition is not harmful in such a distillation because the gas oil is to be subsequently cracked. In

TABLE 80.—VISCOSITY-BREAKING TESTS

Stock	Cracking temp., deg. F.	A.P.I.		Viscosity			Pour-point, deg. F.		Distillate	
		Before	After	Before	Test method	After	Before	After	Per cent	A.P.I.
Fuel oil	830	26.3	25.9	18	Furol at 122	14.2	55	0	18.0	45.0
Residual fuel oil	845	18.8	18.5	193	Furol at 122	49.0	65	55	21.6	46.8
Gas oil	840	25.3	18.5	337	Say. at 100	253.0	75	15	38.2	49.9
Gas oil	837	25.3	24.2	337	Say. at 100	108.0	75	0	17.0	58.4
Reduced crude	850	22.0	28.4	92	Say. at 210	.....	87	..	0.0	

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[16] Tests by Dr. S. Born and the author in the laboratories of the University of Tulsa, 1933.

this way a 70 per cent yield of 14 A.P.I. gas oil has been obtained[17] from an 8 to 10 A.P.I. residue. This was accomplished by heating the stock to about 900°F. in a pipestill heater and flashing the heated oil in a simple fractionating tower. The residue was a brittle bituminous material which could be powdered and fired as a fuel. The same results, if accomplished by vacuum or steam, would be uneconomical. Such units are simple distillation equipments differing from normal topping stills only in the design of the furnace, which should be designed for a somewhat mild rate of heating.

Reforming must be practiced in order to dispose of the large bulk of low octane-number straight-run gasoline or naphtha that is obtained during the topping of crude oil. Straight-run gasoline has an octane number of about 50; cracked gasoline about 70; and the average gasoline now marketed is nearly 70. Thus, polymerization, reforming of naphthas, and the use of tetraethyl lead are necessary. Yields by reforming are higher than from regular cracking-stocks, being 60 to 85 per cent for stocks ranging from kerosene to gasoline. However, the yield is not entirely dependent on the charge-stock because the yield may be greatly changed by the extent of cracking that is practiced. As an example, Egloff and Nelson[18] report the following commercial results when cracking 17.9 A.P.I. topped Smackover crude oil at 200 lb. per square inch and at 935°F.

Gasoline			Residue			Gas and loss, per cent
Yield	A.P.I.	Octane-number	Yield	A.P.I.	Universal Saybolt vis. and 122°F.	
39.0	57.1	80	58.4	8.7	159	2.6
45.2	57.0	80	48.0	4.8	357	6.8
48.8	55.3	80	46.0	2.6	637	5.2
50.2	55.6	80	44.8	0.7	1,411	5.0
63.1	55.1	80	None	Coke	.....	36.9 (and coke)

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[17] Viscosity Breaker, *Ref. Nat. Gaso. Mfr.*, July, 1932, p. 431.

[18] Cracking Light and Heavy Oils, 3d Midyear Meeting, A.P.I., Tulsa, May, 1933.

These data are not for a reforming operation, but they do indicate the effect of the amount of cracking that is practiced. These authors conclude that it is not economical to top the light gasoline and reform the naphtha separately, because the yields and the octane number are substantially the same if the entire gasoline is reformed. These results are not entirely in agreement with the results of LeRoi and Ferguson (page 293).

LeRoi and Ferguson[19] conclude that the yield of a given octane-number product is greatest by a once-through operation, *i.e.*, by passing the stock through a heating coil only. Smaller yields are obtained in passing the stock through a coil and soaker, and still smaller yields are obtained by recycling. They find the capacity of a given equipment is greater at higher pressures.

TABLE 81.—YIELDS BY REFORMING

Stock	A.P.I.	Octane number of stock	Cracking temp.	Cracking pressure	Yield gaso.	Octane No. of gaso.	Process	Reference
Pa. gasoline	58.7	40	....	.....	83.7	76	Dubbs	20
Pa. naphtha	52.7	30	....	.....	84.4	76	Dubbs	20
Pa. kerosene	46.1	..	....	.....	81.2	75	Dubbs	20
Naphtha Cracked naphtha	47–50	..	1010	350	....	72	Quench process*	
Cracked naphtha	......	..	998	350	....	69	Quench process*	
Cracked naphtha	......	..	1010	330	....	70	Quench process*	
Naphtha	51.0	..	925	1,000	82.0	70	Tube and Tank	21
Pa. gasoline	64.6	50	1000	400	76.7	75	Dubbs	18
Pa. naphtha	54.9	31	950	500	73.5	76	Dubbs	18
Joiner and E. Tex. gasoline	58.7	56	950	500	84.4	75	Dubbs	18
Joiner and E. Tex. naphtha	58.7	56	950	500	88.1	71	Dubbs	18
E. and W. Tex. gasoline	61.3	59	995	450	85.8	73	Dubbs	18
M.C. gasoline	59.8	42	975	500	82.3	70	Dubbs	18
M.C. naphtha	53.5	34	1000	500	75.5	75	Dubbs	18
W. Tex. gasoline	58.1	61	950	750	87.4	78	Dubbs	18
W. Tex. naphtha	51.5	52	950	750	80.4	78	Dubbs	18

* Separate reforming coils.

Data on the yields by reforming are given in Table 81. Goldtrap[22] also reports higher yields of a given octane-number gasoline when higher pressures are used. A discussion of the octane number obtained by reforming will be found in Chap. XVII.

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[19] Developments in Naphtha Reforming . . . , 3d Midyear Meeting, A.P.I., Tulsa, May, 1933.

[20] EGLOFF and NELSON, *Oil Gas J.*, Jan. 7, 1932, p. 22.

[21] MCCONNELL, E. B., *Ref. Nat. Gaso. Mfr.*, May, 1931, p. 95.

[22] Increasing Octane Values . . . , *Ref. Nat. Gaso. Mfr.*, April, 1932, p. 281.

Economic Feasibility of Coking.—The feasibility of conducting any or all of the types of decomposition such as reforming and viscosity breaking is an economic problem that depends to a large extent upon market conditions. One of these processes, however, *viz.*, coking, is somewhat isolated from particular conditions and hence will bear special study. Its position of importance lies largely in the fact that it may be used to alleviate a distressed fuel oil market by eliminating excess fuel oil stocks into gasoline products. In order to conduct coking rather than to sell fuel oil directly, the value of gasoline must be as large as or larger than the figures given in Table 82. A complete study of the factors involved is given in the original reference.[23] This table indicates clearly that coking is not a profitable operation unless the price of fuel oil is very low or unless the gasoline price is very high. One factor, the value of coke, is not mentioned in Table 82. A value of $1.50 per ton was used (50 cts. over the cost of removal and storage); and hence if the market value is $2.00 or $3.00 per ton, the values of gasoline given in the table will be greatly lowered. Costs of operating and constructing cracking units are given by Smoley[15] and others.[24]

TABLE 82.—MINIMUM VALUE OF GASOLINE BELOW WHICH COKING IS AN UNPROFITABLE OPERATION (1936)

Value of fuel oil, cts. per bbl.	Minimum market value of gasoline, cts. per gal.		
	10 A.P.I. charge-stock	13 A.P.I. charge-stock	16 A.P.I. charge-stock
20	9.8	6.0	4.7
30	13.0	9.1	6.9
40	high	12.2	9.1

The Houdry Process.—This process is the outstanding example of the so-called catalytic cracking processes. Most catalytic processes have been developed for handling particular hydrocarbons, whereas this process takes all the hydrocarbons in a wide-boiling-range stock and converts them into an unusually uniform gasoline product regardless of the type of raw stock that is handled. The octane number of the gasoline is about 79 by the C.F.R. motor method (about 95 by the 1939 C.F.R. research method), and the yield is 44 to 46 per cent gasoline based on the charge to the catalyst (once-through) whether the raw stock is a light distillate or a heavy one.[25] The success of the process, aside from the high degree of mechanical ingenuity involved, is due primarily to the following factors:

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[23] NELSON, W. L., Coking and Cracking, *Ref. Nat. Gaso. Mfr.*, March, 1936, p. 85.

[24] NELSON, W. L., *Oil Gas J.*, Apr. 6, 1939, p. 55; and Mar. 23, 1939, p. 80.

1. By means of a large once-through yield, the bulk of material that must be handled by the more expensive method of recycling in a thermal process is greatly reduced.
2. No heavy residue is produced, and hence the fuel oil market is relieved.
3. The gasoline has a high octane number and an exceptionally high (octane) blending value.

The charge-stocks now recommended[26] consist of distillate materials from any source, including gas oils from cracked tars or coking chambers. Low-carbon residue materials are most suitable. The flow (Fig. 163) is similar to a high-temperature distillation system but having chambers and their appurtenances for contacting the vapor with the catalyst. Should distillate materials constitute the charge-stock, the tar separator shown in Fig. 163 can be dispensed with. The vapor in the presence of process steam is admitted to the chambers at about 840°F., and passage through the chamber is continued for about 10 min. By this time the pores and surface of the catalyst have been covered with a thin film of carbon and the catalyst must be regenerated. The entire cycle is about as follows:

1. Onstream—10 min.
2. Oil and vapor purge by venting to a condenser and steam jet evacuation system—5 min.
3. Regeneration with preheated air—10 min.
4. Air purge by steam jet ejectors—5 min.

All operations are automatic, even to the opening and closing of valves. Air is supplied by a centrifugal multistage compressor directly coupled to a gas turbine. The compressed air (350°F.)

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[25] WILCOX, O. W., Houdry Catalytic Processes . . . , *World Petroleum*, Annual Refinery Issue, 1939.

[26] Much of the data given here and later were part of a private communication from the E. B. Badger & Sons Co. and the Houdry Process Corporation, 1940.

at 50 lb gage pressure is preheated to 700 to 800°F. and admitted to the chambers. The flue gases issue from the chamber at 850 to 950°F., having absorbed enough heat energy to operate the gas turbine used in compressing the air.

During this cycle the heat of reaction must be provided during the onstream phase and the heat generation during regeneration or burning with air must be removed. These conditions are met by recycling a mixture of molten salts which tends to keep the reaction temperature up to about 850°F. and the regeneration temperature down to 950°F. The net result is an excess of heat which may be used to produce high-pressure superheated steam. About 150,000 B.t.u. per barrel of charge to the catalyst is available for steam generation. The low pressure of 7 to 15 lb. maintained on the chambers during operation is a distinct advantage over the common thermal cracking process which must operate at 200 lb. and up.

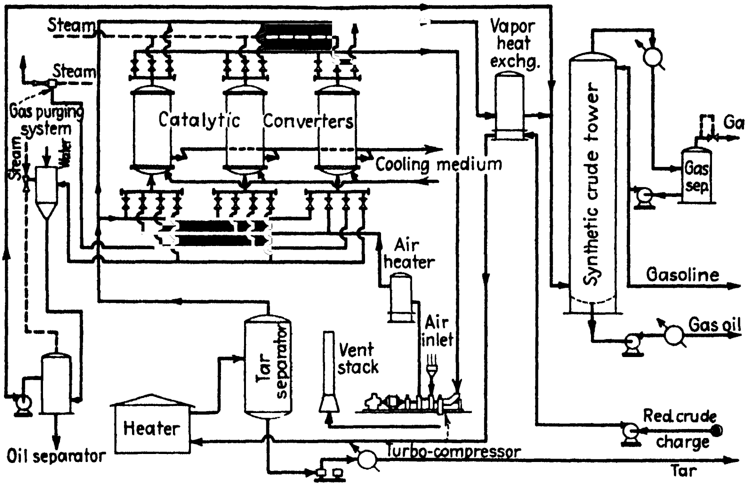

FIG. 163.—Houdry catalytic cracking process.

The chambers resemble a condenser in which the catalyst is packed around the tubes. The vapor passes on the outside of the tubes and through the catalyst, and the recycling molten salt flows through the tubes for purposes of heating or cooling. The tubes have metal fins on the outside which extend to within about an inch of all parts of the catalyst mass.

Clay catalysts having a base of hydrated silicate of alumina to which has been added small amounts of metallic oxides are widely used because of their ruggedness and long life. More active catalysts comprising nothing but compounded materials are also available. The amount of catalyst required is indicated in Table 83, which shows yields as a percentage of the yields when using 1 bbl. of catalyst for 1 bbl. of liquid oil per hour. Temperature (810 to 880°F.) has little effect on the yield of gasoline, but the octane number (C.F.R. 1939 research method) is increased by four to six points at the higher temperatures. Process steam decreases the activity of the catalyst, but it is used as a means of controlling the extent of the reaction. New catalyst is very active; and as its activity decreases, the amount of process steam can also be reduced. Increase in pressure (15 to 85 lb. abs.) produces an increase in gasoline yield, but the gas and coke formation increases even more rapidly. Thus, high pressures are not widely used. The more active the catalyst the greater the yield of gasoline, but the coke and gas formation increases more than proportionally. The catalyst lasts more than 6 months and frequently more than a year.

TABLE 83.—EFFECT OF FLOW RATE ON YIELD
Using clay catalyst

Rate, bbl. oil per hr. through 1 bbl. of catalyst	Yields as percentage of yields at 1 bbl. of oil per bbl. of catalyst			
	Total liquid recovery	Gasoline	Coke	Gas
0.6	92.5	117	160	153
0.8	97.0	109	115	119
1.0	100.0	100	100	100
1.2	101.5	91	89	86
1.5	103.0	79	77	70

Yields[25] are indicated in Table 84. The Houdry gas oil is an excellent charge-stock for thermal cracking. Thus, the Houdry process is used in connection with thermal cracking equipment for handling gas oil and with coking plants for handling heavy straight-run residues.

The catalyst renewal cost amounts to about 2.5 cts. per barrel of capacity based on a change of catalyst every 6 months. The cost of operation is less than for thermal cracking, but the initial investment in equipment is so great that only large plants are built.

TABLE 84.—YIELDS AND PRODUCTS BY HOUDRY PROCESS

	50–94.6% cut of Mirando crude 17.2 A.P.I.	East Texas gas oil 35.7 A.P.I.		Reforming naphtha 46.8 A.P.I.	
Light gasoline, per cent by volume	.....	36.5	.....	58.75	
Gasoline, per cent by volume	49.4	.....	39.1	....	83.42
Motor naphtha, per cent by volume	.....	10.4	50.2	21.40	
Gas oil, per cent by volume	51.0	39.1	11.4	9.10	9.10
Total liquid	100.4	86.0	101.7	89.25	92.52
Dry gas, weight per cent	4.9	13.7	5.4	12.14*	8.22*
Catalyst carbon, weight per cent	4.4	5.4	.....	1.71*	1.71*
Gasolines, A.P.I	53.4	65.7	64.4	60.1	57.8
Gasolines, end-point, deg. F	420	340	392	328	392
Gasolines, octane No. (M.M.)	79	80.6	80.9	77.6	76.5
Motor naphtha, A.P.I	.....	38.3	38.3	39.5	
Motor naphtha, initial deg. F	.....	320	320	311	
Motor naphtha, end-point, deg. F.	.....	452	452	416	
Gas oil, A.P.I	17.8	32.7	32.7	25.2	25.2
Gas oil, initial, deg. F	441	440	440	412	412
Gas oil, end-point, deg. F	728	692	692	694	694

* Fuel oil equivalent—not weight per cent.

The Hydroforming Process.—This catalytic hydrocarbon-reforming process promises competition with the Houdry process, but as yet details of operation have not been disclosed.[26a] The process operates on low-octane-number naphthas, producing 77–80 octane-number gasoline in yields of 80 per cent. It differs little from thermal reforming except that the product does not require chemical treatment and it contains scarcely any olefin hydrocarbons. Naphtha is heated to the reaction temperature and mixed with a similarly handled recycle gas (containing some hydrogen). The mixture is then sent through catalyst chambers and thence through the customary train of equipment, such as a vessel for the separation of recycle gas, a stabilizer tower for the elimination of the gas product, and a tower for separating the gasoline and bottoms. It is a once-through operation except for the recycling of gas.

[26a] SMITH and MOORE, First Commercial Hydroforming Plant Now in Operation, *Oil Gas J.*, Mar. 27, 1941, p. 87; and HIGHTOWER, J. V., First Hydroformer Unit Put On Stream, *Ref. Nat. Gaso. Mfr.*, May, 1941, p. 153.

The hydrogen and recycle gas appears to function as an agent for controlling the reaction so that scarcely any olefin hydrocarbons are produced. The lack of these very reactive hydrocarbons (olefins) may account for the relatively long cycle of operation before coke or carbon dulls the activity of the catalyst. Two catalyst chambers are provided and, while one is being used, the other is revived by burning the carbon from the surface of the catalyst by the passage of a hot stream of flue gas containing a small amount of oxygen. The gasoline consists of 40 to 50 per cent of aromatic hydrocarbons, which would indicate simultaneous reactions of decomposition (cracking), dehydrogenation of ring structures, hydrogenation of olefins, and perhaps isomerization and alkylation.

POLYMERIZATION

The fundamental theory underlying the polymerization process has been discussed in Chaps. XVII and XVIII. The feed-stock for such processes consists of olefin hydrocarbons; and except for the relatively small amounts of olefin gases that are available from cracking-still gas, the feed-stock for polymerization processes must be produced in a preliminary operation of decomposition or dehydrogenation (refer to Fig. 97, Chap. XVII). The cost of producing olefin hydrocarbons from saturated hydrocarbons has been a deterrent to the adoption of polymerization processes, and it also accounts for the attention that is now being centered on alkylation processes. In these, only half as much olefinic material is required in the feed-stock as compared with polymerization, and hence much of the expense of decomposition or dehydrogenation may be avoided.

The thermal process of polymerization is favored for large-scale operations based on butanes as a feed-stock, because having once attained the high temperature required for decomposition, the polymerization reaction can be conducted at little expense by simply holding the decomposed stock for a few minutes before cooling it. The optimum operating conditions for decomposition and polymerization are not exactly the same, but from an economic standpoint it has been found that the two processes can be successfully conducted in a single operation of heating. Catalytic polymerization is most widely used for handling gases that are already rich in olefin gases, *i.e.*, in connection with cracking plants. The catalytic processes are also better adapted to small-scale operation.

As yet, catalytic dehydrogenation has not been applied widely on a commercial scale. The development of such processes will instigate a wholesale development of commercial polymerization, alkylation, and related chemical processes.

Thermal Polymerization.—This process is so intimately related to the process of thermal decomposition that most commercial flow diagrams show both processes—in fact, the flow diagrams are devoted more to decomposition and product recovery than to polymerization. Inasmuch as antiknock properties are the primary superiority of polymerized gasoline, branched-chain hydrocarbons (mainly isobutane) are preferred as a feed-stock because they yield high octane-number polymers. Propane is not used as a feed-stock because of the high pressures and temperatures that must be employed, although it usually constitutes a portion of the recycling stream of a polymerization plant.

TABLE 85.—STOCKS AND PRODUCTS OF POLYMERIZATION PLANT*

Mol per cent	Fresh feed	Furnace feed	Residue gas		Light poly. gaso.	Heavy poly. gaso.	Gas oil and tar
Methane	...	.....	51.0	Gravity, A.P.I.	75	44	20
Ethane	...	1.5	28.0	I.B.P., deg. F.	90	195	370
Propane	...	10.5	19.5	F.B.P., deg. F.	245	450	(90% at
Isobutane	20	30.0	1.5	Per cent at 158 deg. F.	58	...	660°F.)
n-Butane	80	58.0		Per cent at 212 deg. F.	95	2–3	
Total	100	100.0	100.0	Reid V.P., lb. per sq. in.	13	2–3	
Unsaturates	15	14.0	12.0	Octane No. (C.F.R. motor method)	77.5	75	
				Octane No. (blending value)	87.0		

* See Fig. 164.

The flow diagram shown in Fig. 164 shows the essential features of the Baytown plant of the Humble Oil & Refining Co.[27] Analy-

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[27] TURNER and RUBEY, Light Hydrocarbons . . . , *Ref. Nat. Gaso. Mfr.*, September, 1938, p. 423.

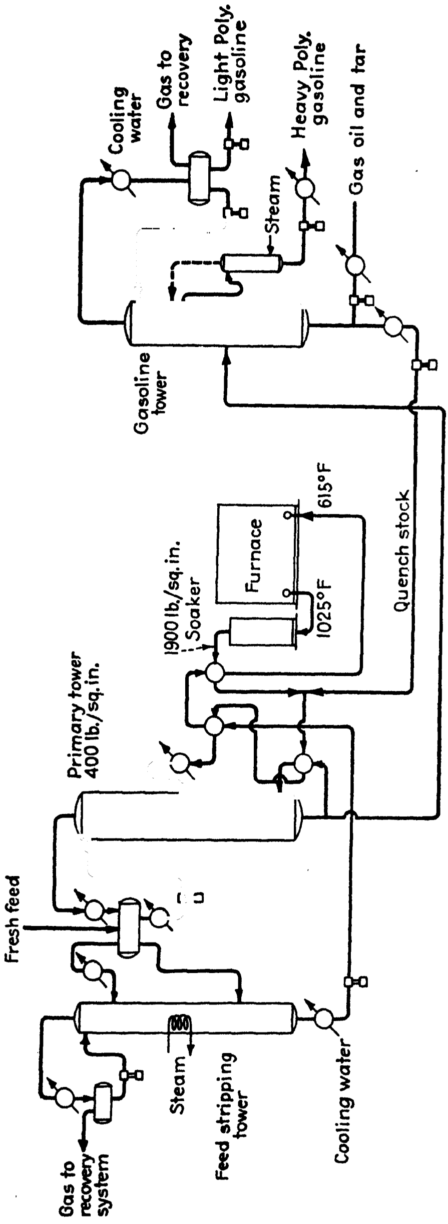

FIG. 164.—Typical thermal polymerization (and decomposition) plant.

ses of the feed and several stocks are shown in Table 85. The capacity of the plant is 10,000 bbl. daily, but the amount of material charged to the furnace is 38,000 bbl. per day. The yield of finished polymer gasoline is 3,500 bbl. per day. The yield of gasoline (10 lb. Reid) decreases with the conversion-per-pass somewhat as follows:

	Yield of polymer, weight per cent		
	5% conversion	10% conversion	15% conversion
Propane	51.7	47.5	
Butane	71.6	64.4	56.7

Note that the conversion-per-pass applies to both the decomposition and the polymerization parts of the still.

Catalytic Polymerization.—The two most successful catalytic processes are those utilizing a solid phosphoric acid catalyst and those using sulfuric acid as a catalyst. Sulfuric acid is also useful in alkylation processes, and to some extent sulfuric acid alkylation is displacing sulfuric acid polymerization. Both of these methods must be used with an auxiliary operation, such as cracking, decomposition, or dehydrogenation, for the production of an olefin-rich feed gas.

The flow diagram of a phosphoric acid polymerization plant is shown in Fig. 165. The equipment consists essentially of a heater and catalyst chambers. The temperature at the outlet of the heater is 340 to 400°F., which is sufficient to maintain an average temperature in the chamber of 400 to 450°F. Higher temperatures must be avoided because at 650°F. the catalyst tends to volatilize, and even at lower temperatures, water vaporizes from the catalyst. Water is sometimes injected in the amount of 5 per cent of the volume of the feed-stock to suppress the vaporization of water from the catalyst, but large amounts of water tend to soften or disintegrate the catalyst into a mud and also to promote the formation of propyl alcohol. A pressure of about 500 lb. per square inch is employed. This serves to reduce the volume of gas that must be handled, to increase the rate of reaction (page 343), and to provide sufficient pressure in the stabilizer to condense liquid propane as a reflux material.

As much as 70 gal. of gasoline has been produced per pound of catalyst, but a large amount of catalyst is employed so that shut-downs for regenerating or replacing the catalyst are infrequent. In studies of polymerization[28,29] the amounts of gas per hour per pound of catalyst ranges from 1.1 to 11.9, but in commercial operations larger amounts of catalyst are used in order to permit long runs. The life of the catalyst is so great that in many smaller plants it is replaced rather than regenerated. Regeneration is conducted by passing air (650°F.) into the chamber at such a rate that the temperature does not exceed 950°F. and then hydrating the catalyst by maintaining an atmosphere of steam for 10 to 16 hr. at approximately 500°F. The conversion of propene and butene to polymer gasoline amounts to about 90 per cent or a yield of about 16 gal. per thousand cubic feet of pure olefin gases. The gasoline has a high octane-blending value,[29] being equivalent to octane numbers of 100 to 125 depending upon the octane number of the low-value blending stock.

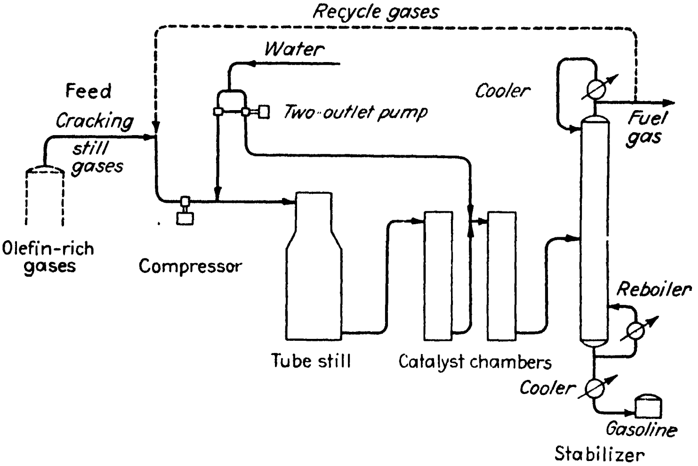

FIG. 165.—Phosphoric acid polymerization. (*Oil Gas J.*)

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[28] EGLOFF, IPATIEFF, and CORSON, Polymerization a New Source of Gasoline, *Ind. Eng. Chem.*, **27**, 1077 (1935).

[29] IPATIEFF and EGLOFF, Polymer Gasolines from Cracked Gases, *Oil Gas J.*, May 16, 1935, p. 31.

The hot acid (sulfuric) polymerization process[30] is used to polymerize butylenes into polymers of the gasoline boiling-range. At lower temperatures only isobutylene is absorbed by 67 per cent acid, and hence the cold-acid process may be used (along with hydrogenation) for the manufacture of isooctane (2,2,4-trimethylpentane). In the hot-acid process, mixed butylenes are polymerized to the extent of 85 to 90 per cent by absorption into 67 per cent acid at a temperature of about 80°C. Polymerization is so rapid at this temperature that the butylenes are scarcely absorbed before polymers are formed. The plant consists of a reaction tower followed by vessels for prolonging the time and acid settlers. The acid is recycled through this part of the system along with the feed-stock and is not consumed except by mechanical entrainment or losses. The polymerized material along with unaffected hydrocarbons is neutralized with caustic soda and sent to a stabilizing column for the separation of raw polymer gasoline and gas. The contact time is between 10 and 15 min. Plain steel and iron equipment is used for the part of the system that is in contact with acid. Excessive corrosion does not take place.

The raw polymer may be treated to remove all sulfur and hydrogenated to give saturated side-chain products similar to isooctane. In the alkylation processes, which are discussed later, hydrogenation is not necessary because the product of the process consists of hydrocarbons that are already saturated with hydrogen.

ALKYLATION

Such processes are more important in many respects than plain polymerization processes. Main among these is the fact that olefin hydrocarbons are expensive to procure as a feed-stock. The alkylation processes require only half as much olefinic material in the feed-stock as polymerization processes. The processes are not yet widely used commercially, but they promise to become very important.

Sulfuric Acid Process.—This process has been applied primarily to mixtures of isobutane and butenes, although other combinations of olefins and isoparaffins can be employed if their use becomes economically advisable. The reaction appears to take place in two steps, the first of which involves the formation of an alkyl ester such as butyl hydrogen sulfate followed by combination of this material with isobutane and the liberation of the acid. The absorption of the olefin hydrocarbon occurs at a rate several hundred times as fast as the absorption of paraffins, and hence in order to maintain the proper concentration of the two hydrocarbons in the acid it is necessary to recycle a large excess of the saturated hydrocarbon through the system as indicated in Fig. 166. The higher the ratio of isoparaffin to olefin in the feed-stock the greater the yield, the higher the octane number, and the smaller the acid consumption,[31] and hence this ratio is always held at 5:1 or higher. Contact times of about 5 min. appear to be satisfactory, but commercial plants are operating at 20 to 40 min. An acid strength of 98 per cent is used, but it becomes diluted during processing to about 90 per cent. The dilution, however, is by absorption of unactive hydrocarbons and certain oxidation products rather than by water. Thus, the spent acid that is currently removed from the process is not destroyed chemically and may be recovered by standard methods or may be used in acid treating other refinery stocks. The make-up acid amounts to 1 to 3 lb. of acid per gallon

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[30] McAllister, S. H., The Catalytic Polymerization of Butylenes by Sulfuric Acid, *Ref. Nat. Gaso. Mfr.*, November, 1937, p. 493.

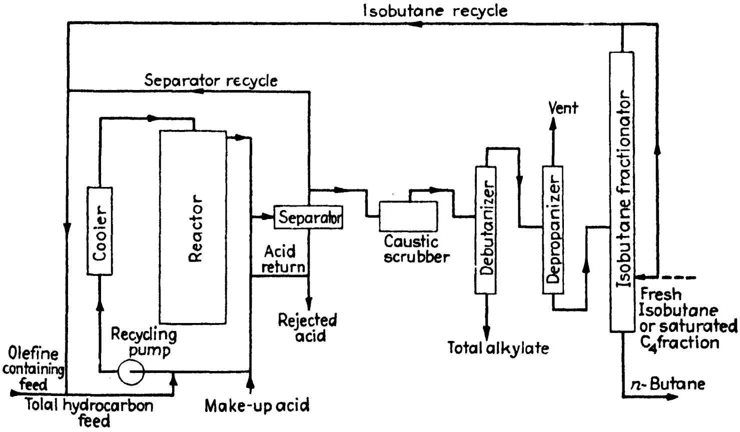

FIG. 166.—Sulfuric-acid alkylation plant. (*Ref. Nat. Gaso. Mfr.*)

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[31] MACKENZIE, K. G. (read by), High Octane Aviation Fuel by . . . . Alkylation Process, *Ref. Nat. Gaso. Mfr.*, November, 1939, p. 494.

of product. From one to two parts of acid are circulated per part of hydrocarbon. Agitation is accomplished by means of jets or baffles. Temperatures of 32 to 50°C. are employed, and a temperature above 70°C. results in excessive acid replacement and a decreased yield of gasoline.

The alkylate product ranges from 185 to 215 per cent based on the olefin part of the feed and of this total alkylate, 75 to 95 per cent is 300°F. end-point aviation gasoline having an octane number (C.F.R. motor method) of 87 to 93.

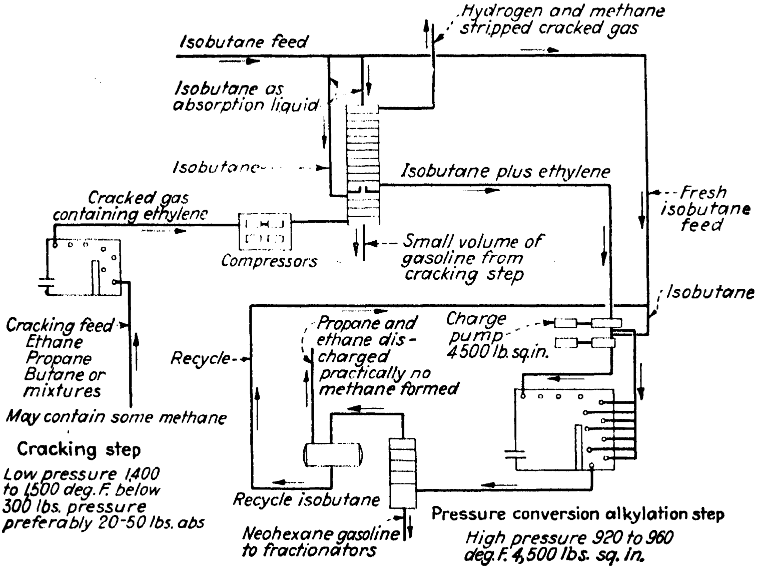
Hydrogen and methane stripped cracked gas
Isobutane feed
Isobutane as absorption liquid
Isobutane
Isobutane plus ethylene
Fresh isobutane feed
Cracked gas containing ethylene
Compressors
Small volume of gasoline from cracking step
Isobutane
Cracking feed
Ethane
Propane
Butane or mixtures
Recycle
Propane and ethane discharged practically no methane formed
Charge pump 4500 lb. sq. in.
May contain some methane
Cracking step
Low pressure 1400 to 1500 deg. F. below 300 lbs. pressure preferably 20-50 lbs. abs
Recycle isobutane
Neohexane gasoline to fractionators
Pressure conversion alkylation step
High pressure 920 to 960 deg. F. 4,500 lbs. sq. in.

FIG. 167.—Thermal alkylation process (neohexane pilot plant). (*Oil Gas J.*)

Thermal Alkylation.—Whereas sulfuric acid alkylation operates most successfully on isobutylene, the butenes, and propylene, thermal alkylation acts most readily on ethylene followed by propylene, butenes, and isobutylene in the order named. A temperature of about 950°F. and a pressure of 3,000 to 5,000 lb. per square inch[32] are required. The olefin-rich charge-stock may be produced by a hydrocarbon decomposition process operating at 1425°F. and at nearly atmospheric pressure. Such conditions are favorable for ethylene formation. The ethylene is absorbed in isobutane for introduction into the alkylation plant. The alkylation furnace handles a recycling stream of isobutane, and the ethylene-isobutane solution is introduced at 10 points in the soaking zone of the furnace. Little tar or material boiling above gasoline is produced because of the low concentration of ethylene in the reaction zone. A general flow diagram of the process is shown in Fig. 167. Times of 2 to 7 sec. are required at 950°F., depending largely on the hydrocarbons being treated and the amount of isobutylene recirculated.

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[32] OBERFELL and FREY, Thermal Alkylation and Neohexane, *Oil Gas J.*, Nov. 23 and 30, 1939, p. 50.

The yield of liquid products, including all hydrocarbons in the boiling-range of gasoline as well as neohexane, is approximately 70 per cent by weight of the net consumption of ethane-propane and isobutane consumed during decomposition and alkylation. As the normally liquid hydrocarbon content of the coil-effluent is increased from 20 to 35 per cent by weight (conversion-per-pass), the neohexane content of these liquids decreases from about 40 to about 30 per cent. In commercial operation it is not feasible to strive primarily for neohexane production, and hence the preceding conversions-per-pass are employed. In theoretical experiments it is possible by using pure charge-stocks and a low conversion-per-pass to obtain liquids that contain more than 60 per cent of neohexane.

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CHAPTER XXV

NATURAL GASOLINE

Casinghead gasoline first attracted commercial attention in about 1904 in the Pennsylvania oil district. By 1920 the value of natural-gasoline products was estimated to be over $75,000,000 per year, but during that year and 1921 the industry suffered a serious relapse because of the general economic stress but more directly because of the unscrupulous sale of casinghead-kerosene blends as gasoline during the previous decade. At that time the manufacturers formed the Natural Gasoline Manufacturers Association and by scientific investigations and publicity have been able to reestablish the respect of the buying public. Properly manufactured natural gasoline has properties that make it of definite usefulness as a motor fuel, particularly when blended with regular gasoline. The low boiling-range of natural gasoline, or its tendency to vaporize easily, makes it an admirable motor fuel for cold weather when ordinary gasoline may fail to ignite properly. However, casinghead or raw natural gasoline contains dissolved gases and is not satisfactory as a motor fuel because the gases are evolved at engine temperatures, causing vapor-lock in the feed system. Today the properties of natural gasoline, particularly the vapor-pressure, are closely regulated, so that the refiner can safely take full advantage of the superior properties of blended motor fuels. Even pure natural gasoline is sold by some refiners as a motor fuel. Furthermore, natural gasoline has a higher octane rating than straight-run gasoline. For several years (1933–1939) the amount of natural gasoline used was about 7 per cent of the total gasoline consumption.

The lighter hydrocarbons such as propane, isobutane, and butane, which may be removed from raw natural gasoline during its processing, are finding a wide use as so-called bottled gas, as stocks for the manufacture of city gas, and as stocks for the hydrocarbon processes discussed in Chaps. XVII, XVIII, and XXIV. During the six years from 1933 to 1939, the production of liquefied petroleum gas increased from 39 to 224 million gallons per year. The liquefied gas is shipped under pressure and is allowed to expand when ready for use. Inasmuch as the heating value of the pure gas is unnecessarily high, it is often mixed with air. The following tabulation[1] indicates the cheapness of butane gas as compared with a normal manufactured gas.

COMPARATIVE PRICES OF BUTANE AND CITY GAS

Cost of Butane at Burner, Cts. per Gal. (Delivered Price)	Equivalent Value of 530 B.t.u. City Gas, Cts. per 1,000 Cu. Ft.
8.0	41.4
6.0	31.0
5.0	25.9
4.0	20.7
3.0	15.5

In 1930 the number of butane-air plants for the manufacture of city gas has been estimated as 60 and as many more were under construction. Commercial butane is also used to enrich the low-heating-value manufactured gases. As well as centralized plants of this kind, many rural dwellers are burning bottled or liquefied gas in kitchen ranges and lamps.

Although the design and operation of natural-gasoline absorption and stabilization plants have been handled largely by production engineers, there is no real difference in principle between these plants and those used in the refinery. The principles underlying all distillation and absorption operations are much the same, and the design of natural-gasoline equipment may be considered as a part of the design fundamentals outlined in previous chapters. However, natural gasoline and natural gas can be accurately analyzed, and hence the design of natural-gasoline equipment can be approached in a more precise manner than the design of heavy oil equipment.

General Processing Plan.—The processing involved in the manufacturing of finished products from natural gas consists mainly of two operations, *viz.*, absorption and stabilization.

1. *Wet* natural gas or a gas containing relatively large percentages of compounds higher in molecular weight than propane is processed to produce *dry* natural gas and *raw, or wild, natural gasoline.* The raw gasoline may be separated from the wet gas by (*a*) adsorption by charcoal, (*b*) compression, (*c*) absorption in a mineral absorption oil, or (*d*) a combination

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[1] OBERFELL, G. G., *Proc.* 10*th Ann. Meeting Nat. Gaso. Mfr.*, 1931.

of the compression and absorption processes. Although all of these processes have been used, most modern plants are combination compression and absorption plants. Modern absorbers operate between 35 and 500 lb. per square inch.

2. Stabilization of the raw natural gasoline. Raw gasoline as obtained above usually contains 10 to 30 per cent methane, ethane, and propane. These dissolved gases cause the gasoline to be highly volatile, and they must be removed before the gasoline can be shipped or marketed as a stable product. Stabilization is nothing more than fractionation for the removal of these light, high-vapor-pressure components. Since the fractionator must be refluxed with almost pure liquid propane or butane, the operation must be conducted under pressure.

The stabilization of wild gasoline by allowing it to stand in open tanks (weathering) is no longer used, because a serious loss occurs by vaporization of gasoline hydrocarbons as well as gas. The removal of gases from any stock by high-pressure fractionation, whether it be wild natural gasoline, casinghead (or drip) gasoline, pressure-still distillate, or the raw products from a hydrocarbon-conversion process (Chap. XVIII), is widely referred to as stabilization. When a single hydrocarbon is removed from a stock, the operation is referred to as depropanization,[2] debutanization, etc. (refer to Fig. 109, page 367).

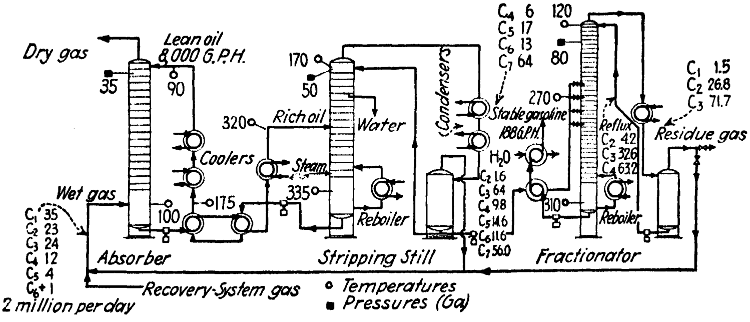

FIG. 168.—Absorber, stripper, and stabilizer.

A simplified flow diagram of the complete absorption, stripping, and stabilization operation is given in Fig. 168. The compressors that are used to create the pressure in the absorption tower are not shown. Figure 120 presents much the same arrangement

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[2] COULTHURST, L. J., Depropanization of Butane, *Oil Gas J.*, July 11, 1940, p. 50.

TABLE 86.—ANALYSES OF GASES

Material	From	Approx. gal. gaso.† per 1,000 cu. ft. of gas	CH_4*	C_2H_6	C_3H_8	C_3H_6	iC_4H_{10}	C_4H_{10}	C_4H_8	iC_5H_{12}	C_5H_{12}	$C_6H_{14}+$	Others
1. Dry gas	Stabilizer	0.0	77.9	10.04	8.61	.....	2.6	0.85					
2. Dry gas	440-lb. absorber	0.13	86.56	8.67	3.92	.....	0.36	0.47	...	0.2			
3. Dry gas	52-lb. absorber	0.06	60.77	19.83	17.12	.....	1.21	0.97	...	0.10			
4. Dry gas	18-lb. absorber	0.0	18.66	27.24	45.10	.....	6.0	3.0					
5. Waste gas	Propane stabilizer	0.0	4.3	82.7	13.0								
6. Dry gas	Compressors and coolers	0.64	81.04	9.74	5.46	.....	1.35	1.3	...	0.5	0.25	0.36	
7. Dry gas	59-lb. absorber	0.13	92.1	1.9	4.5	.....	0.6	0.7	0.2				
8. Dry gas	53-lb. absorber	0.25	76.7	10.5	8.8	.....	1.1	0.5	0.4				
9. Dry gas	An average of 45‡	0.10	85.9	6.31	7.74	.....	0.78	0.69	0.16				
10. Dry cracked gas	Stabilizer	0.13	64.5	16.0	6.7	1.9	2.9		1.3	0.6			H_2 2.9, C_2H_4 2.9
11. Dry cracked gas	Gyro	1.48	38.81	13.15	3.68	13.5	.....	6.43	...	2.47			C_2H_4 20.31
12. Dry cracked gas	Gyro absorber	....	44.4	10.3	2.95	12.0	.....	.....	...	....	....	.....	C_2H_4 30.35
13. Wet ref. gas	Vapor recovery	3.19	46.78	16.51	18.8	.....	4.44	7.77	...	2.76	1.51	1.43	
14. Wet ref. gas	Raw gaso. tanks	4.87	7.17	15.21	34.72	.....	10.88	23.16	...	4.29	3.02	1.55	
15. Wet ref. gas	Vapor recovery	3.70	41.62	20.91	19.72	.....	9.05		4.43			2.09	H_2S 2.18
16. Bottle-gas feed	Stabilizer reflux	....	1.4	7.4	87.4	.....	2.1	1.7					
17. Wet natural gas	2,400-lb. distillate well	2.13	88.56	4.8	2.11	.....	0.61	0.63	...	0.49	0.24	2.56	
18. Wet natural gas	An average of 45‡	1.78	79.8	6.48	6.22	.....	1.35	2.33	...	2.97			
19. Wet cracked gas	15-lb. separator	5.06	33.1	21.8	16.7	4.5	7.1		2.8	5.5		3.3	Air 3.1, C_2H_4 1.3
20. Wet cracked gas	Gyro stabilizer	1.20	11.37	12.35	.....	44.87	13.86			1.99			C_2H_4 15.56
21. Poly plant feed	Cracking	....	19.80	19.80	18.20	19.40	1.5		5.6	0.80			C_2H_4 14.9
22. Waste poly gas	Catalytic polymerizer	0.0	26.40	26.50	19.40	7.20	30		0	....	....	....	C_2H_4 17.5

* N_2, CO_2, O_2, etc., usually counted as CH_4.

† 26–70 grade.

‡ The wet gases of 18 yielded the dry gases of 9.

except that control instruments are shown. The wet gas is compressed and admitted to an absorber column. This column and also the stripper and stabilizer are of the conventional bubble-plate type of construction, although the tray spacing is usually not over 18 in. In the absorber the wet gas flows countercurrently to an absorption oil and leaves the top as a dry natural or refinery gas. The rich absorption oil flows through exchangers in which heat is exchanged with the hot lean absorption oil, through a steam heater, and into the stripping column. Some fractionation as well as stripping may be accomplished in the stripper or still, and hence heat is supplied at the bottom by a steam reboiler and reflux is used at the top. Wild, or raw, natural gasoline and steam pass overhead, and some of the light constituents cannot be condensed. These are cycled back into the absorber. The wild gasoline is pumped through heat exchangers to the stabilizer (fractionator or rectifier), and stable natural gasoline and dry gas are produced. The stabilizer is a typical fractionating column with a steam reboiler. Sometimes it is more economical to allow some gasoline hydrocarbons to escape in the residue gas from the stabilizer and cycle this gas through the absorber than to do an exact job of fractionation in the stabilizer.

Natural and Refinery Gases.—Almost all of these gases are of such a composition that they can be profitably processed for the manufacture of natural gasoline. Prior to 1915 a gas containing less than 7 gal. of stable natural gasoline per thousand cubic feet was called a dry gas and in general was not considered as suitable for processing. Since that time the value of natural gasoline has increased and the methods of recovering the gasoline have been so improved that almost all natural gas containing more than 2 gal. of gasoline per thousand cubic feet is being processed and gases that contain only 0.3 gal. per thousand cubic feet may be economically handled. Table 86 shows analyses of various natural and refinery gases.

Brewster[3] reports analyses of refinery gases from topping, cracking, rerunning, and coke stills. The crude oil contained 30 per cent gasoline, and an additional 30 per cent gasoline was produced by cracking. About 20 per cent of the original oil was coked. Table 87 shows the composition and amounts of these gases.

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[3] *Oil Gas J.*, June 19, 1930, p. 46.

TABLE 87.—AMOUNT AND COMPOSITION OF REFINERY GASES

	Crude stills	Coke stills	Dry gas from cracking	P.D. release gas	Auto tar plant	P.D. rerun stills	Total
Cu. ft. per bbl. of crude	7	26	100	37	20	10	200
Approximate mol. wt.	51	32	23.8	40.5	28.2	52	31
Approximate gal. C_5 + per 1,000 cu. ft.	7.4	5.1	0.8	3.5	1.2	8.2	2.5
Analysis:							
CH_4	5	47	68	18	53	4	49.13
C_2H_6	12	15	15	24	20	10	16.81
C_3H_8	30	16	11	31	16	30	17.46
C_4H_{10}	34	9	4	18	8	35	10.23
C_5H_{12}+	19	13	2	9	3	21	6.37

In estimating the gasoline content of a wet gas the following tabulation will be of value. The figures represent the approximate number of gallons of liquid that can be obtained from 1,000 cu. ft. of each of the compounds.

Ethane	25.2	Hexane	41.1
Propane	27.4	Heptane	46.4
Isobutane	32.4	Octane	51.4
Butane	31.6	Pentanes and heavier	41.5
Pentanes	36.4	Hexanes and heavier	45.0

For the olefin hydrocarbons the foregoing figures may be reduced by about 10 per cent. Propane is not considered as a recoverable gasoline product unless bottled gas is to be manufactured.

Example 75. Gasoline Content of Natural Gas.—A wet gas contains 30 per cent butanes, 5 per cent pentanes, and 2 per cent hexanes and heavier. Basis: 1,000 cu. ft. of the natural gas.

Gal.

Gasoline from butanes $= \frac{30}{100} \times \cancel{1{,}000} \times \frac{31.8}{\cancel{1{,}000}} = 0.3 \times 31.8 = 9.54$

Gasoline from pentanes $= 0.05 \times 36.5 = 1.83$

Gasoline from hexane plus $= 0.02 \times 45.0 = .90$

Pentanes plus $= 2.73$

Yield of 26–70 grade gasoline $= \frac{2.73}{0.68} = 4.01$ gal. per 1,000

Some butanes would be available for bottle gas, etc.

Table 89 indicates the analyses of common gasoline products. Commercial butane, bottle gas, and pressure distillate are also shown.

Properties of Natural Gasoline.—Natural gasoline has a higher octane number than normal straight-run gasoline. Alden[4] finds that the antiknock properties of natural gasoline can be best correlated against vapor-pressure. Table 88 shows the approximate relationship between octane number and Reid vapor-pressure for Mid-Continent natural gasolines.

TABLE 88.—OCTANE-NUMBER VERSUS REID VAPOR-PRESSURE

Reid Vapor-pressure at 100°F.	Octane Number, Original Waukesha Unit, 212°F. Jacket
4	57.3
10	64.6
14	69.6
18	73.3
22	76.2
26	78.4
30	80.0

Alden also finds that the octane number of natural gasoline is increased more by the addition of a given amount of tetraethyl lead than are the octane numbers of other gasolines. Furthermore, the octane number of natural gasoline is decreased less, when the engine jacket temperature is increased from 212 to 350°F., than the octane number of other gasolines, and this is particularly true when compared with the decrease for cracked fuels.

Specifications.—The official specifications of the Natural Gasoline Manufacturers Association of America (1940), are as follows:

1. Reid vapor-pressure	10 to 34 lb.
2. Percentage evaporated at 140°F	25–85
3. Percentage evaporated at 275°F	Not less than 90
4. End-point	Not higher than 375°F.
5. Corrosion	Noncorrosive
6. Doctor test	Negative, "sweet"
7. Color	Not less than plus 25 (Saybolt)

In addition to the foregoing, natural gasoline is divided into 24 possible grades on a basis of vapor-pressure and percentage evaporated at 140°F. These grades are shown in Fig. 169.

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[4] *Oil Gas J.*, Jan. 21, 1932, p. 22.

TABLE 89.—ANALYSES OF GASOLINE PRODUCTS

Material	From	A.P.I.	V.P., lb. per sq. in.	Analysis, per cent by volume (gas)							
				CH_4	C_2H_6	C_3H_8	iC_4H_{10}	C_4H_{10}	iC_5H_{12}	C_5H_{12}	$C_6H_{14}^+$
1. Raw gasoline	Absorber	94.5	....	0.08	1.51	12.12	8.76	29.33	48.2		
2. Raw gasoline	Absorber	....	....	....	1.83	12.57	32.75		29.98		22.87
3. Raw gasoline	High-press. abs.	92.2	60	0.03	2.27	17.29	9.38	23.33	47.7		
4. Raw gasoline	High-press. abs.	92.2	50	0.04	1.78	16.03	8.81	26.95	5.54	12.24	28.61
5. Raw gasoline	High-press. abs.	91.8	51	....	1.9	17.08	10.23	25.54	45.25		
6. Raw gasoline	Absorber	....	....	....	0.72	13.69	4.74	23.71	10.43	21.19	25.07
7. Raw pressure distillate	150–200 lb. separator	....	....	0.91	3.08	6.71	8.74		8.36		72.2
8. Raw pressure distillate	25-lb. separator	....	....	....	0.73	3.16	6.06		6.36		83.69
9. Raw pressure distillate	Cross	....	....	....	0.35	2.36	5.66		6.7		84.93
10. Raw pressure distillate	Holmes Manley	....	....	0.45	3.7	6.31	7.62		8.5		73.42
11. Stabilized gasoline	Stabilizer	85.6	....	....	....	0.10	0.10	32.6	67.2		
12. Stabilized gasoline	Stabilizer	89.0	29	....	....	0.11	32.94		40.07		26.88
13. Stabilized gasoline	Stabilizer	77.8	18.7	....	....	.....	1.02	17.55	13.67	15.06	52.7
14. Stabilized gasoline	Stabilizer	78.7	17.2	....	....	.....	1.73	16.13	11.58	19.33	51.23
15. Stabilized gasoline	Stabilizer	74.7	11.5	....	....	.....	.....	9.97	90.03		
16. Stabilized gasoline	Stabilizer	....	....	....	....	0.51	4.42	24.06	13.18	18.19	39.64
17. Stabilized gasoline	175-lb. stabilizer	77.0	18.4	....	....	.....	2.67	19.17	18.80	13.27	46.09
18. Commercial butane	Stabilizer	0.581*	....	....	0.04	3.32	18.1	75.8	2.74		
19. Commercial butane	245-lb. stabilizer	....	62.0§	.....	....	.....	58.20	41.20	0.6		
20. Commercial propane†	Stabilizer	....	......	.....	2.0	98.0					
21. Commercial propane	440-lb. stabilizer	....	216.0§	.....	0.20	99.40	0.40				
22. Distillate	525-lb. separator	....	......	15.31	4.61	5.63	3.58	5.74	6.42	3.68	54.94‡

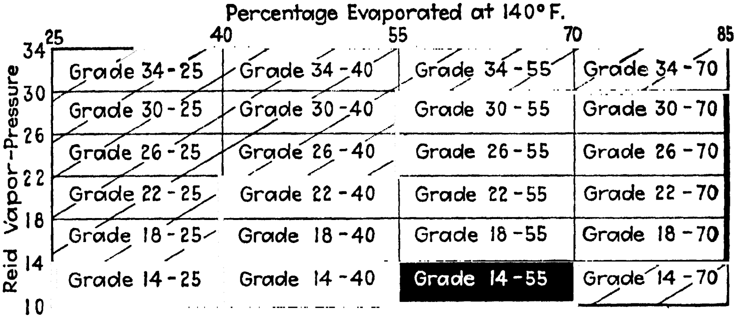
* Specific gravity 60/60.

† Per cent liquid volume.

‡ Heptane plus, 42.14 per cent.

§ At 105°F.

The grades of gasoline that are widely used fall within the 13 grades outlined in Fig. 169. The approximate compositions of the different grades of gasoline can be estimated from Fig. 170. The use of this figure can be best illustrated by means of an example.



34	Grade 34-25	Grade 34-40	Grade 34-55	Grade 34-70
30	Grade 30-25	Grade 30-40	Grade 30-55	Grade 30-70
26	Grade 26-25	Grade 26-40	Grade 26-55	Grade 26-70
22	Grade 22-25	Grade 22-40	Grade 22-55	Grade 22-70
18	Grade 18-25	Grade 18-40	Grade 18-55	Grade 18-70
14	Grade 14-25	Grade 14-40	Grade 14-55	Grade 14-70

FIG. 169.—Grades of natural gasoline. The most common grades are outlined in the block.

Example 76. Relation of Composition and Physical Properties of Natural Gasoline (Fig. 170).—A natural gasoline has a Reid vapor-pressure of 16; it contains no propane; and 50 per cent of it distills at 140°F. What are its approximate composition, its gravity, and the percentage evaporated at 100°F.?

The percentage evaporated at 140° is located along the base line, and the vapor-pressure is located among the Reid vapor-pressure axes on the right, using the 0 per cent propane axis. These two lines cross at the circle point on the diagram. This intersection point is then located with respect to the other axes in the figure, giving properties as follows:

A.P.I. gravity	79.2 (curved lines reading along base and to right)
Per cent evaporated at 100°F	18.5 (rather flat curving lines reading to right)
Per cent butanes and lighter	13.5 (horizontal lines reading at left)
Per cent pentanes in pentanes and heavier	35.5 (converging straight lines reading at top)

ANALYSIS

Propane	0.0	Pentanes (35.5%)	30.7
Butanes	13.5	Hexanes+ (100 − 35.5)	55.8
Pentanes+	86.5		86.5

Tentative specifications for the liquefied petroleum gases propane and butane are given by Legatski.[5] The vapor-pres-

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[5] *Oil Gas J.*, May 19, 1932, p. 44. Tests are described.

GRAPHICAL ANALYSIS OF NATURAL GASOLINE

The basic relationship shown in this chart is betwpen the four following factors:

Title	Description	Coordinates
% evaporated @ 100°F.	A.S.T.M. Engler distillation	Dashed almost horizontal curves
% evaporated @ 140°F.	A.S.T.M. Engler distillation	Solid vertical lines
% butanes and lighter (volume)	Includes propane, etc.	Light dashed horizontal lines
Pentane ratio	Per cent pentanes (volume) in pentanes and heavier	Dashed almost vertical lines

The intersection of the lines representing the known data is also an intersection of the lines representing the data to be estimated. Thus the intersection of 40 "% evaporated at 100°F." with 65 "% evaporated at 140°F." is also the intersection of 26.8 "% butanes and lighter" and 42.3 "pentane ratio."

In addition to this basic relationship, the following factors may be estimated, preferably with the basic relationship as the starting point:

Title	Description	Coordinates
A.P.I. gravity		Solid curves, almost 45° slope
Reid vapor pressure	For 0 to 3.0% propane	
% propane (by volume)	If known factors are the distillation data, the actual R.V.P. must be known	Solid lines at side of chart

The point established by the basic relationships also establishes these three items, with the proviso noted for "% propane." Thus in the above example the gravity would be 85.3° A.P.I.; the Reid vapor pressures at 0, 1, 2 and 3% propane would be 23.0, 25.0, 27.0 and 29.0 lb. respectively. If the actual Reid vapor pressure had been 26.0 lbs., the propane content would be estimated at 1.5%.

In general, knowing any two factors, all the others can be determined except for those relationships which include the effect of propane content, in which cases either the propane content or the actual Reid vapor pressure must be known. Also conclusions based on gravity as one of the two known factors will not be so accurate as otherwise.

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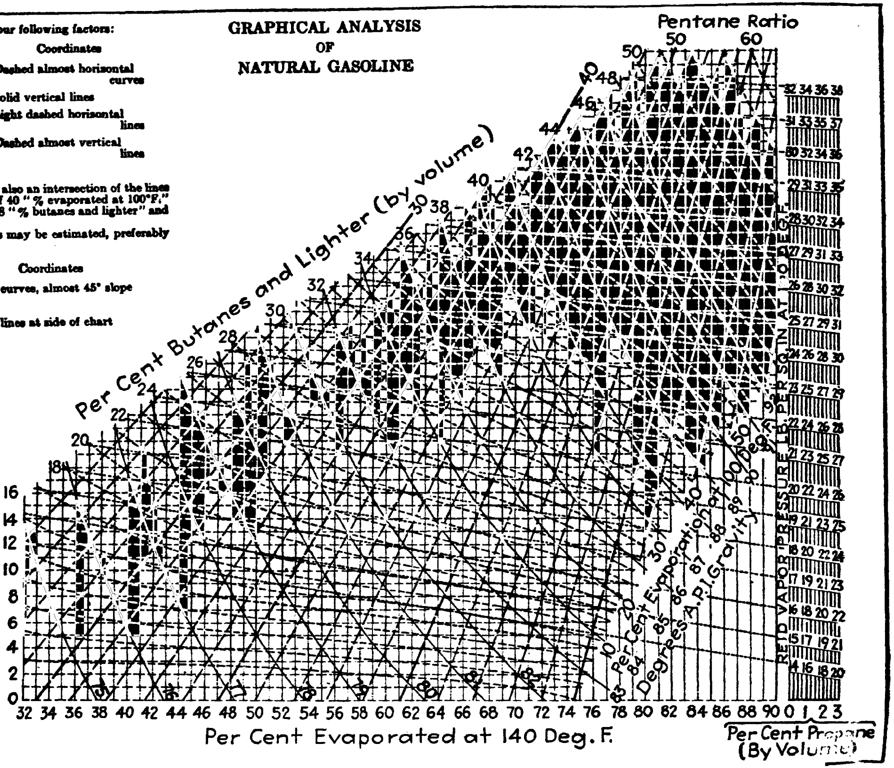

sure specifications are limited to some extent by the vessels (tanks and cylinders) that are available for transportation. The water content must be limited because the water becomes frozen and clogs the vaporizing apparatus during expansion. The water that is permitted amounts to about 10 parts of water vapor per million. The sulfur content is listed as two groups of compounds, because sulfide stenches are often used to impart a characteristic odor to the gas so that leaks can be located.

Blending of Natural Gasoline.—The composition of natural gasoline greatly affects its vapor-pressure. This is inferred in Figs. 169 and 170. The reason for the powerful effect of composition on vapor-pressure is the great differences in the vapor-pressures of the low-boiling components. The vapor-pressure of propane is very high, and hence a small amount of propane will greatly increase the total vapor-pressure. If butane is substituted for propane (by good fractionation), the resulting gasoline has a much lower vapor-pressure. These relations are given graphically by Kremser.[6] Figure 171 shows the gallons of a heavier hydrocarbon component that may be substituted for a gallon of a lighter component without changing the vapor-pressure of the total material.

For each gallon of propane that is present in a 14-lb. gasoline, about 5.35 gal. of butane or 3.5 gal. of isobutane may be substituted for the propane without changing the vapor-pressure (Fig. 171). Stated in the reverse, this means that the total yield of 14-lb. gasoline can be increased by about 4.35 and 2.5 per cent respectively by substituting butane or isobutane for propane. However, butane and isobutane must be available in sufficient quantity in the raw gasoline. Thus a thorough elimination of the lightest component of a raw gasoline by good fractionation in the stabilizer is a profitable operation unless the separation is a particularly difficult one. For summer blending requirements a high-pentane-content gasoline is desirable, but during the winter a high-butane gasoline may be used.

The Reid vapor-pressure is slightly lower than the true vapor-pressure because of inadequacies of the Reid test. This discrepancy is a function of several variables and hence can be given in only an approximate way. The true vapor-pressure is 5 to 9 per cent higher than the Reid vapor-pressure.

[6] Midyear Meeting, A.P.I., Tulsa, June 3, 1932.

The boiling-range of naphtha and natural-gasoline blends can be closely approximated by averaging the material boiling up to a given temperature, in the ratio of the quantity of each blending agent that is used. The method is exact for fractionating distillations, but it is not perfect for distillations such as the A.S.T.M. distillation. If the entire distillation range is desired, the calculations can be more easily accomplished by graphical methods. The curve of the blend will be spaced from the curves of the two blending stocks by a distance along the percentage axis that is inversely proportional to the amount of each blending agent.

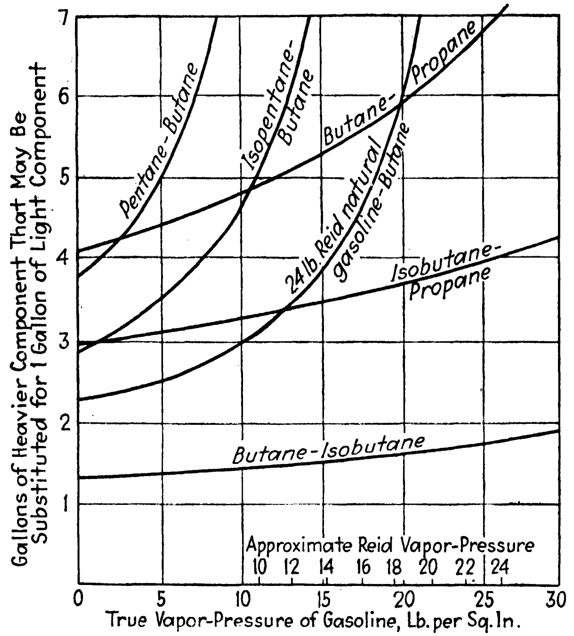

FIG. 171.—Amount of a natural-gasoline component that can be substituted for another component without changing the vapor-pressure. (*Kremser, Oil Gas J.*)

Example 77. Boiling-range of Blends.—A naphtha contains 18 per cent of material boiling to 200°F., and a natural gasoline, 70 per cent. If the two stocks are blended 20:80, *i.e.*, 20 volumes of natural gasoline to 80 volumes of naphtha, how much of the blend will distill at 200°?

$$\begin{array}{rl} & \text{Per Cent} \\ 0.80 \times 18 = & 14.4 \\ 0.20 \times 70 = & \underline{14.0} \\ \text{Material boiling to } 200^\circ = & 28.4 \end{array}$$

An illustration of the graphical method is not justified, but the following equations will clarify the operation to be followed in a graphical solution.

$$\text{Per cent in blend, boiling to } 200^\circ = 18 + {}^{20}\!/_{100}(70 - 18) = 28.4$$

or

$$\text{Per cent in blend, boiling to } 200^\circ = 70 - {}^{80}\!/_{100}(70 - 18) = 28.4$$

The vapor-pressure of blends can be estimated in much the same manner except that mol percentages rather than volume percentages must be used. The method is accurate when true vapor-pressures are used, but it is not exact when using the Reid vapor-pressure.

Example 78. Vapor-pressure of Blends.—Naphtha and natural gasoline are to be blended. The properties of the stocks are

Stock	Vapor-pressure	A.P.I.	Lb. per gal.	Molecular weight
Naphtha	6	57	6.25	119
Natural gasoline	18	72	5.79	90

What is the vapor-pressure of a 20:80 blend?
Basis: 1 gal. of blend.

		mols	mol per cent
Naphtha	$\frac{0.8 \times 6.25}{119}$	= 0.042	76.5
Nat. gasoline	$\frac{0.2 \times 5.79}{90}$	= 0.0129	23.5
		0.0549	100.0

Partial vapor-pressure of naphtha .... $0.765 \times 6 = 4.6$
Partial vapor-pressure of nat. gasoline... $0.235 \times 18 = 4.2$
Vapor-pressure of blend = 8.8 lb. per sq. in.

The specific gravity (not A.P.I.) of blends is also proportional to the amount of each stock in the blend and the gravities of the stocks. The octane number of blends is not usually directly proportional to the amounts and octane numbers of the two stocks. If, however, the two stocks are very similar, as two natural gasolines or straight-run gasoline and natural gasoline, the octane number can be computed with fair accuracy. Polymerized, cracked, and certain special gasoline stocks, when used in blends, behave as if they have very high octane numbers.

NATURAL-GASOLINE PLANT DESIGN AND OPERATION

Although the design of natural-gasoline absorbers, strippers, and stabilizers (fractionators) is essentially the same as the design methods outlined in other chapters, the mechanism of handling these computations is facilitated because an exact analysis, showing the percentage of each hydrocarbon, is usually available. However, the computations are involved because so many components must be handled at the same time.

Raoult's law and Dalton's law are the basis for most of these computations. These laws are discussed in detail on pages 227–229 and in Example 40. At high pressures Raoult's law is not valid, and equilibrium constants must be used. These constants are presented in Figs. 70–74 and are discussed on pages 230–232 and in Example 41. Computations of the equilibrium relations of complex mixtures such as natural gasoline are involved because of the many components. These relations are discussed on pages 238–240 and Example 42. The fundamentals of fractionation, absorption, and stripping are discussed in Chap. XV.

Absorbers and Strippers.—The performance of absorbers can be most easily understood by means of a mathematical study.[7] In an equilibrium plate the relation between the composition of the vapor leaving the plate and the liquid overflowing from the plate may be expressed as follows:

$$y_n = Kx_n \tag{32}$$

in which y_n is the mol fraction of a particular component in the vapor leaving any plate or the nth plate; x_n is the mol fraction in the overflow liquid; and K is a constant that may be determined from Figs. 70–74 or by Raoult's law.

By a material balance (Fig. 88)

$$L(x_n - x_{n-1}) = V(y_{n+1} - y_n) \tag{96}$$

in which L is the total mols of pure absorber oil; V is the total mols of dry gas; the subscript $n - 1$ refers to the plate above the nth plate; and $n + 1$ to the plate below.

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[7] SOUDERS and BROWN, *Ind. Eng. Chem.*, **24**, 519 (1932).

Substituting $\frac{y_n}{K}$ for x_n, and $\frac{y_{n-1}}{K}$ for x_{n-1},

$$\frac{L}{KV}(y_n - y_{n-1}) = y_{n+1} - y_n \tag{97}$$

The factor L/KV is commonly referred to as the *absorption factor*.

Let

$$A = \frac{L}{KV} = \text{absorption factor} \tag{98}$$

Solving Eq. (97) for y_n and substituting Eq. (98),

$$y_n = \frac{y_{n+1} + Ay_{n-1}}{1 + A} \tag{99}$$

For a *single-plate absorber:*

$$y_1 = \frac{y_2 + Ay_0}{1 + A} \tag{100}$$

in which y_1 is the mol fraction of the component in the gas that leaves the top plate of the absorber and y_0 is the mol fraction of the component in the gas that is in equilibrium with the entering oil (or the oil flowing from the hypothetical zero plate which is above the top plate).

For a *two-plate absorber:*

$$y_2 = \frac{y_3 + Ay_1}{1 + A}$$

Substituting the value of y_1 and solving for y_2,

$$y_2 = \frac{y_3(A + 1) + A^2y_0}{A^2 + A + 1}$$

For a *three-plate absorber*,

$$y_3 = \frac{y_4(A^2 + A + 1) + A^3y_0}{A^3 + A^2 + A + 1}$$

or

$$y_3 = \frac{\dfrac{(A^3 - 1)}{(A - 1)}y_4 + A^3y_0}{\dfrac{(A^4 - 1)}{A - 1}}$$

or

$$y_3 = \frac{(A^3 - 1)y_4 + A^3(A - 1)y_0}{A^4 - 1}$$

For an *absorber with n plates,*

$$y_n = \frac{y_{n+1}(A^n - 1) + A^n(A - 1)y_0}{A^{n+1} - 1} \tag{101}$$

and because

$$y_n = Kx_n$$

$$x_n = \frac{y_{n+1}(A^n - 1) + A^n(A - 1)y_0}{K(A^{n+1} - 1)} \tag{102}$$

A material balance over the entire absorber gives

$$A(y_n - y_0) = y_{n+1} - y_1 \tag{103}$$

Solving Eq. (103) for y_n and setting it equal to y_n from Eq. (104),

$$y_1 = y_{n+1}\left(\frac{A - 1}{A^{n+1} - 1}\right) + y_0\,\frac{(A^{n+1} - A)}{(A^{n+1} - 1)} \tag{104}$$

in which y_{n+1} is the mol fraction of the component in the entering rich gas or gas arising from the hypothetical plate below the bottom or n plate.

This is a general statement of the absorption equation that was derived by Kremser,[8] although the formulation herein given was published by Brown.[7] The equation may be arranged in a more convenient form thus:

$$\frac{A - 1}{A^{n+1} - 1} = 1 - \frac{A^{n+1} - A}{A^{n+1} - 1}$$

Rearranging Eq. (104),

$$\frac{y_1 - y_{n+1}}{y_0 - y_{n+1}} \quad \text{or} \quad \frac{y_{n+1} - y_1}{y_{n+1} - y_0} = \frac{A^{n+1} - A}{A^{n+1} - 1} \tag{105}$$

where $(y_{n+1} - y_1)$ = actual change in composition of gas.
$(y_{n+1} - y_0)$ = maximum change in composition of gas that would occur if an infinite number of plates were used or if the gas leaving the top of the absorber were in equilibrium with the lean oil.

An equation for stripping can be derived in a similar manner:

$$\frac{x_e - x_n}{x_e - x_{n+1}} = \frac{S^{n+1} - S}{S^{n+1} - 1} \tag{106}$$

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[8] *Nat. Petroleum News,* May 21, 1930, p. 43.

where x_n = mol fraction of component in liquid leaving stripper (lean).

x_e = mol fraction of component in liquid entering stripper (rich).

$$S = \frac{KV}{L} = \frac{1}{L/KV} = \frac{1}{A}. \tag{107}$$

If steam is used for stripping, as is the case in gasoline plant strippers, $x_{n+1} = 0$ and Eq. (106) reduces to

$$\frac{x_e - x_n}{x_e} = \frac{S^{n+1} - S}{S^{n+1} - 1} \tag{108}$$

These two fundamental equations [Eqs. (105) and (106)] are expressed graphically in Fig. 172. The figure may be used by determining the value of the factor $(y_{n+1} - y_1)/(y_{n+1} - y_0)$, or $(x_e - x_n)/x_e$, and noting the value of A (or S). The quantity of absorption oil or steam may be obtained from A or S as explained in the following paragraph.

Absorption and Stripping Factors.—The common method of expressing the amount of absorption oil is gallons of oil per thousand standard cubic feet of gas (60°F., 14.7 lb.). With these units the absorption factor can be expressed as follows:

$$A = \frac{L}{KV} = \frac{3.156dG}{KM} \tag{109}$$

or if Raoult's law holds

$$A = \frac{3.156dG\pi}{PM} \tag{110}$$

where d = sp. gr. of absorption oil.

G = gal. of absorption oil per 1,000 cu. ft. of gas.

K = equilibrium constant (Figs. 70–74).

M = molecular weight of absorption oil.

P = vapor-pressure of component, lb. per sq. in. abs.

π = total pressure in absorption tower, lb. per sq. in. abs.

The stripping factor may be expressed in a similar manner.

$$S = \frac{1}{A} = \frac{KV}{L} = \frac{KWM}{150d} \quad \text{or} \quad \frac{PWM}{150d\pi} \tag{111}$$

in which W is the pounds of steam per gallon of oil.

In determining the oil-to-gas ratio for an absorber, it is necessary to decide how much of a certain low-boiling component (usually butane) can be allowed in the final gasoline and to compute the absorption factor and the oil circulation for this component. The other components will also be absorbed and to varying extents, depending upon their vapor-pressures or equilibrium constants. The amount of absorption is inversely proportional to the vapor-pressure [Eqs. (109) and (110)]. Thus the absorption factor is different for each component even though the oil circulation is the same for all. For several components, *i.e.*, 1, 2, 3, etc.,

$$A_1 : A_2 : A_3 = \frac{1}{K_1} : \frac{1}{K_2} : \frac{1}{K_3} \tag{112}$$

After the A for the governing or key component is determined, the values of A and the amount of absorption of each of the other components can be obtained from Eq. (112). The reverse is true of stripping; *i.e.*, the amount of stripping is directly proportional to the vapor-pressure of the component in question. For an absorption factor of 1 ($A = 1$) for normal butane, the factors for other components in a low-pressure absorber are about as follows:[8]

Component	Absorption Factor A
C_3H_8	0.25 of factor for butane
iC_4H_{10}	0.67 of factor for butane
C_4H_{10}	1.0 of factor for butane
iC_5H_{12}	2.67 of factor for butane

This relation is only approximate because it varies with temperature.

The full significance of the factor $(y_{n+1} - y_1)/(y_{n+1} - y_0)$ in Fig. 172 is frequently overlooked. The expression $y_{n+1} - y_1$ is nearly equal to the amount of component that is removed from the gas; *i.e.*, it is the difference between the concentration in the incoming and outgoing gas.[9] The expression in the denominator, $y_{n+1} - y_0$, represents the maximum amount of component that could be removed if the outgoing gas were in equilibrium with the incoming lean oil. If the absorption oil contains none of the component under consideration, *i.e.*, $x_0 = 0$ (therefore $y_0 = 0$),

[9] It is not exactly equal to the amount of component removed because the total number of mols of gas changes as it passes through the absorber (Example 28, page 191). If the compositions were given as mols of component per mol of dry gas, then the expression would exactly represent the mols of component removed per mol of dry gas.

the factor $(y_{n+1} - y_1)/(y_{n+1} - y_0)100$ is nearly[9] equal to the percentage recovery of the component in the absorber. For practical purposes, it may be considered as the fraction of the component that is absorbed. Likewise, $(x_e - x_0)/x_e$ is nearly[9] equal to the fraction of the component that is removed from the oil by the stripper. Thus if we desire to absorb 99 per cent of the isopentane from a gas, the value of $(y_{n+1} - y_1)/(y_{n+1} - y_0)$ is nearly 0.99, if the lean oil contains no isopentane. Or if we wish to strip 99 per cent of a component from the oil with steam, the value of $(x_e - x_n)/x_e$ is nearly 0.99. The application of Fig. 172 to the design or analysis of an absorber is by no means as complicated as the mathematical derivation herein presented. The use of Fig. 172 can be most ably presented by means of the examples which follow this discussion.

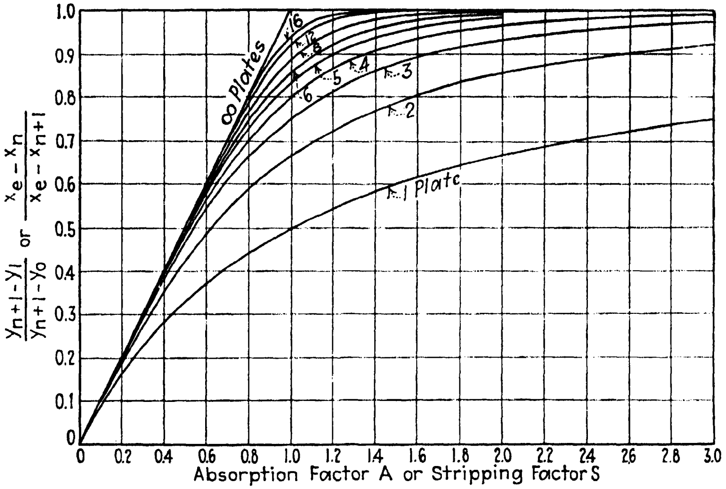

FIG. 172.—Relation of number of equilibrium plates to absorption and stripping factors. (*Dr. G. G. Brown and Ind. Eng. Chem.*)

An examination of Fig. 172 shows the relation between the absorption factor and the percentage of component that is absorbed. Consider the line for five theoretical plates (Fig. 172). This line approaches the line for infinite plates as the absorption factor is decreased, until at 50 per cent absorption, or $(y_{n+1} - y_1)/(y_{n+1} - y_0)$, the value of A is nearly 0.5 (about 0.505). In other words, at low percentages absorbed, the percentage absorption and the absorption factor are numerically the same. The number of plates that are used also affect the location of the point at which A is substantially equal to the percentage absorbed. Likewise the number of plates is related to the absorption factor that must be used to absorb substantially all of a component. These relations are somewhat as follows:

No. of theoretical plates	Fraction below which the absorption factor and the fraction absorbed are equal*	Absorption factor* required to absorb about 99% of a component
1		
2	0.1	
3	0.3	
4	0.4	3.0
5	0.5	2.2
6	0.55	1.9
8	0.6	1.5
12	0.7	1.3
16	0.8	1.2

* Approximate.

The optimum value of the absorption factor A for any particular plant is primarily a function of the value of gasoline and the cost of recirculating oil. The absorption factor (or oil recirculation) increases rapidly as large percentages of the key component are absorbed. In most situations the economical amount of key component to absorb is between 90 and 95 per cent[10] rather than the 99 per cent value that is so frequently employed. The economical recovery of key component may be as low as 60 to 70 per cent if the price of gasoline is low, if the cost of oil recirculation exceeds about 4 cts., or in small refinery installations.

Example 79. Oil Rate for Low-pressure Absorber.—A 26–70 grade of finished gasoline is to be produced from a gas of the following composition:

Component	Volume Per Cent
C_3H_8	7.15
iC_4H_{10}	1.39
C_4H_{10}	2.55
iC_5H_{12}	1.34
$C_5H_{12}+$	1.98

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[10] NELSON, W. L., Economy in Natural Gasoline Plant Operation, *Ref. Nat. Gaso. Mfr.*, May, 1936, p. 167.

The absorber is to operate at 90°F. and at a pressure of 50 lb. per sq. in. abs. The absorption oil has a specific gravity of 0.83 and a molecular weight of 160. The oil is completely stripped of isopentane, but it contains 0.0005 mol fraction of pentane plus. The absorber has 16 actual plates.

How much oil should be recirculated, and what will be the approximate composition of the raw gasoline?

A 26–70 grade of gasoline will contain about 33 per cent butanes and lighter. If 99 per cent of the isopentane is absorbed, enough butanes will be absorbed to provide the 33 per cent that is required in the finished gasoline (Fig. 170).

Considering isopentane (key component),

$$y_1 = \text{mol fraction in residue gas} = \frac{0.01 \times 0.0134}{(1 - 0.0134) + 0.01 \times 0.0134} = 0.000136$$

$$\frac{y_{n+1} - y_1}{y_{n+1} - y_0} = \frac{0.0134 - 0.000136}{0.0134 - 0} = 0.9898$$

For practical calculations it is customary to use the value of

$$(y_{n+1} - y_1)/(y_{n+1} - y_0)$$

as the percentage absorbed, or in this case 99 per cent.

If the plate efficiency is 50 per cent, the column will behave as if it consisted of eight theoretical plates. The absorption factor, to recover 99 per cent of a component, when eight plates are used, is about 1.5 (Fig. 172). The equilibrium constant for isopentane at 90°F. and 50 lb. is about 0.37 (Fig. 73).

$$\text{Gal. oil per } 1{,}000 = \frac{AKM}{3.156d} = \frac{1.5 \times 0.37 \times 160}{3.156 \times 0.83} = 33.8$$

The equilibrium constant for butane is about 0.9 (Fig. 72), and hence the absorption factor for butane is

$$A_{\text{butane}} = 1.5 \frac{0.37}{0.9} = 0.615$$

Component	Mol fraction	Gal. per 1,000 cu. ft.	Equi. constant at 90° and 50 lb.	Absorption factor	Percentage of each component that is absorbed (Fig. 172)	Gal. absorbed per 1,000 cu. ft.	Percentage composition of raw gasoline
C_3H_8	0.0715	1.9	2.8	0.2	20	0.38	16.35
$i\text{-}C_4H_{10}$	0.0139	0.45	1.2	0.46	46	0.206	9.0
C_4H_{10}	0.0255	0.8	0.9	0.615	61	0.488	21.0
$i\text{-}C_5H_{12}$	0.0134	0.5	0.37	1.5	99	0.495	21.35
C_5H_{12} plus	0.0198	0.75	0.24	2.3	100	0.75	32.3
						2,319	100.00

and the absorption of butane (Fig. 172) is about 61 per cent. The gallons of butane absorbed per 1,000 cu. ft. are

$$0.0255 \times 31.4 \times 0.61 = 0.488$$

All of the components were studied in the same manner, as shown in the table on page 563.

The analysis of the raw gasoline is not exact because some of the propane and butanes will be lost in the stripper and a little ethane (neglected) will be present in the raw gasoline.

The approximate analysis of the finished stable gasoline can be estimated as follows:

Gal. of pentanes and heavier. . . . . $0.495 + 0.75 = 1.245$

Gal. of butanes. . . . . $1.245 \times \frac{0.33}{0.67} = 0.613$

Excess butanes. $(0.206 + 0.488) - 0.613 = 0.081$ gal.

ANALYSIS OF STABLE GASOLINE

Component	Gal.	Percentage, liq. vol.
Butanes	0.613	33.0
Isopentane	0.495	26.6
Pentanes+	0.75	40.4
Recovery of 26–70 gasoline	1.858	100.0

Gasoline strippers or stills are primarily fractionators, and hence the methods of design are chiefly those given in Chap. XXIII. For this reason, no illustration of stripping tower calculations will be given, but in general the methods employed are the same as those outlined in Example 79.

High-pressure Absorbers.—High-pressure absorbing equipment is being more and more widely used. The reasons for this trend are as follows: (1) The amount of absorption oil is decreased, and (2) the capacity of the absorber column is increased. However, these two savings must pay for the additional cost of compression and for the extra cost of the high-pressure equipment.

The effect of pressure on the oil recirculation can be illustrated by a study of the absorption equation [Eq. (109) or (110)]. Raoult's law is not greatly inaccurate up to pressures of 80 lb. abs., and hence changes in K or P are eliminated if Raoult's law is assumed to be valid. This leaves only two variables in Eq. (110), the pressure and the oil recirculation. For a given absorption oil, a fixed number of plates, a constant temperature, and a fixed recovery (or value of A), the relation of oil recirculation to pressure is an inverse function.

Thus the recirculation at 80 lb. in terms of the recirculation at 35 lb. is approximately

$$G_{80} = {}^{35}\!/_{80}G_{35} = 0.437G_{35}$$

At higher pressures the foregoing does not hold because two factors are variables [Eq. (109)]. The oil recirculation is directly proportional to K, but K is dependent on the pressure. As an example, the values of K at 35 and 500 lb., for pentane, are about 0.3 (at 85°F.) and 0.07 (at 95°F.) respectively. Thus if 50 gal. is required at 35 lb., only 11.2 gal. is required at 500 lb.—and only 3.5 gal. would be required if Raoult's law is assumed to be valid.

It will be noted that a higher absorption temperature was used at 500 than at 35 lb. So much gasoline is absorbed in a small amount of oil, in the 500-lb. absorber, that the latent heat of condensation becomes an important factor and raises the oil temperature. In ordinary absorbers little or no rise in oil temperatures occurs; but in high-pressure absorbers or when a very rich gas is absorbed at a low pressure, the temperature rise amounts to 10 to 20°F.

In designing high-pressure columns only one major difference arises. The computation is conducted as in Example 79 except that some gasoline is condensed during compression to the high pressure. Equation (35) (page 240) can be used to determine the amount condensed, and the method of computation is much the same as given in Example 42.

Example 80. Condensation during Compression.—A lean natural gas is to be compressed from 30 to 500 lb. per sq. in. abs. and cooled to 80°F. before it enters the absorber. The analysis of the gas is

CH_4	78.8
C_2H_6	6.5
C_3H_8	6.2
iC_4H_{10}	1.4
C_4H_{10}	2.3
iC_5H_{12}	1.6
$C_5H_{12}+$	3.2

What is the final composition of the gas and condensate and the amount of condensate?

Basis: 100 mols or volumes of gas.

Equation (35) must be solved by trial and error because V (or C) is not known until the computation is complete.

A value of V is assumed; C is found from V; and Eq. (35) is filled in. The solution of the equation gives the actual V; and if it is not the same as the assumed value, a new assumption must be made.

As an example, the values for methane in the table will be computed:

Assume $V = 96$, then $C = (100 - V)$ or 4.

$$\frac{C}{V} = \frac{4}{96} = 0.0416$$

K_1 for CH_4 at 80° and 500 lb. (Table 32) is 6.5.

$$K_1G_1 = 6.5 \times 78.8 = 512.2$$

$$\frac{C}{V} + K_1 = 0.0416 + 6.5 = 6.542$$

$$\frac{K_1G_1}{\frac{C}{V} + K_1} = \frac{512.2}{6.542} = 78.29 \text{ volumes of } CH_4 \text{ uncondensed}$$

The other hydrocarbons were computed in a similar manner as shov in Table 90. Upon totaling the volumes of each of the hydrocarbons, column (6), the total is 96.02 rather than 96 as assumed. A second solution would have been necessary had the sum been in error by more than about 0.1 per cent.

TABLE 90.—TRIAL-AND-ERROR SOLUTION FOR EXAMPLE 80

(1) Component	(2) Values of G, mols	(3) Values of K at 500 lb. and at 80°F.	(4) $K \times G$, (2) × (3)	Assume $V = 96$, $\frac{C}{V} = 0.0416$		(7) Mols gaso. (2) − (6)
				(5) $\frac{C}{V} + K$	(6) Values of V, (4) ÷ (5)	
CH_4	78.8	6.5	512.2	6.542	78.29	0.51
C_2H_6	6.5	1.2	7.8	1.242	6.27	0.23
C_3H_8	6.2	0.46	2.85	0.502	5.68	0.52
iC_4H_{10}	1.4	0.22	0.31	0.262	1.18	0.22
C_4H_{10}	2.3	0.16	0.368	0.202	1.82	0.48
iC_5H_{12}	1.6	0.071	0.114	0.113	1.01	0.59
$C_5H_{12}+$	3.2	0.052	0.166	0.094	1.77	1.43
Total	....	.....	....	.....	96.02	3.98

The compositions of the residue gas and the condensate are as follows:

Component	Mols, or volume per cent	
	Residue gas	Condensate gasoline
CH_4	81.53	12.80
C_2H_6	6.53	5.78
C_3H_8	5.91	13.08
iC_4H_{10}	1.23	5.53
C_4H_{10}	1.91	12.06
iC_5H_{12}	1.05	14.82
$C_5H_{12}+$	1.84	35.93

The residue gas, as shown above, is the material that would be processed in a 500-lb. absorber.

Construction of Absorbers and Strippers.—The diameter of an absorber can be determined by the methods outlined in Chap. XXIII. The linear velocities that are used are usually lower than for other bubble-towers. There are several reasons for the low velocity:

1. The temperature is low (increases density).
2. The trays are usually closely spaced.
3. Entrainment is kept at a minimum.
4. The pressure is relatively high (increases density).
5. The oil rate is high.

The most important of these, in reducing the velocity, is probably the high oil rate. Kallam and Steward[11] report that the allowable velocity for low-pressure absorbers decreases with the oil-to-gas ratio approximately as follows:

Oil-to-gas Ratio, Gal. per 1,000	Velocity, Ft. per Sec.
10	1.0
20	0.9
50	0.7
100	0.5
500	0.2
1,000	0.12

They do not state if different towers were used or if the downspouts were increased in size to care for the additional oil circulation.

[11] *Ref. Nat. Gaso. Mfr.*, November, 1929, p. 62.

The details of tray design, tray spacing, etc., were discussed in Chap. XXIII.

Stabilizer Design.—No entirely satisfactory methods of determining the number of plates to use in a stabilizer or fractionator are available. All involve trial-and-error computations; and if the inadequacy of the equilibrium constants is considered, perhaps all that is justified in the way of computations is the use of the infinite reflux fractionating equation [Eq. (83), page 498]. A comparison of the computed analyses of an overhead distillate[12] by actual reflux and by assuming infinite reflux shows:

Component	Experimental	Actual reflux	Infinite reflux
CH_4	2.58	2.56	2.58
C_2H_6	13.35	13.34	13.68
C_3H_8	78.20	78.46	79.20
iC_4H_{10}	5.27	5.45	4.40
C_4H_{10}	0.35	0.19	0.14
iC_5H_{12}	0.25*	trace	trace

* Probably an error in analysis.

The method of determining the number of plates is discussed in Chap. XXIII.

Stabilizers are built with a large number of trays (often more than 30) and for high reflux rates (often a reflux ratio of more than 8:1). If designed in this manner, the unit will be flexible enough to take care of almost any condition that may arise. In fact, a stabilizer is frequently operated for the production of several gasolines of greatly different vapor-pressures, and hence a flexible unit is exactly what is needed.

The pressure at which a stabilizer should operate can be estimated by trial and error. The partial-vapor-pressure of a component in the liquid reflux is equal to the partial-pressure of that component in the outgoing gas:

$$y = Kx \qquad (32)$$

The gas composition can be computed by a material balance involving the feed and the desired stable gasoline. When the proper pressure is assumed, the values of the K's in Eq. (32)

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[12] NELSON, W. L., Nat. Gaso. Stabilizer Fractionation, *Oil Gas J.*, Oct. 20, 1938, p. 59.

will be such that the sum of the mol fractions in the liquid (*X*'s) will be equal to 1.0. Example 81 illustrates this calculation.

Example 81. Stabilizer Pressure and Composition of Reflux. A raw gasoline has the following composition:

CH_4	0.03	iC_4H_{10}	9.38
C_2H_6	2.27	C_4H_{10}	23.33
C_3H_8	17.29	$iC_5H_{12}+$	47.77

A 26–70 grade of gasoline is to be produced. The temperature of the cooling water is 83°F., and hence the condenser temperature will be about 90°F. What is the approximate fractionator pressure?

A 26-70 grade of gasoline contains about 30 per cent butane. The mols and mol fractions of the components in the residue gas are about as follows:

Component	Moles	Approximate mol per cent in residue gas
CH_4	0.03	0.09
C_2H_6	2.27	7.1
C_3H_8	17.29	54.21
i and *n* C_4H_{10}	12.3*	38.6
Total	31.89	100.0

* *i* and *n* C_4H_{10} = (9.38 + 23.33) − (47.7 × $^{39}/_{70}$).

y = *Kx*, for each component. If the proper pressure is used, the sum of the *x*'s is equal to 1 (Figs. 70–74 and Tables 32, 33).

(1) Component	(2) Vapor *y*	Assume 150 lb.		Assume 100 lb.		Assume 65 lb.	
		(3) *K* at 90°	(4) (2) ÷ (3)	(5) *K* at 90°	(6) (2) ÷ (5)	(7) *K* at 90°	(8) (2) ÷ (7)
CH_4	0.0009	20	0.00004	30			
C_2H_6	0.071	3.5	0.202	5	0.142	8	0.087
C_3H_8	0.5421	1.1	0.492	1.5	0.361	1.9	0.285
C_4H_{10}	0.386	0.38	1.015	0.5	0.773	0.65	0.594
Total	......	.....	1.709	....	1.276	....	0.966

The final assumption can be more easily estimated by interpolating or extrapolating than by reading new values of *K*, because the charts cannot be read accurately.

$$\text{Pressure} = 100 - \frac{1.276 - 1.0}{1.276 - 0.966}(100 - 65) = 69.0 \text{ lb.}$$

The pressure is greatly increased if the condenser temperature is 100 rather than 90°.

The composition of the reflux, as mol percentage, is given in column (8) of the tabulation.

The bottom temperature can be computed in a manner similar to that used in Example 81. For this situation, however, the sum of the *partial-vapor-pressures* (atmospheres) or *Kx*'s should be equal to 1.0. The temperature is varied until the *Kx*'s are such that the sum is equal to 1.0. In fact, the same general type of computation may be used at many points such as the gas separator vessel, the top plate, or the feed plate and may even be used in working from plate to plate throughout the tower to determine the number of plates that are required. At many points in the tower, however, the method is very complicated, because reflux constitutes a part of the material at the plate.

References

(Earlier references are given in the First Edition of this book)

NORMAN, H. S.: . . . Butane Propane Unit . . . , *Oil Gas J.*, July 1, 1937, p. 28.

RAGATZ and McFADDEN: Absorption-plant Cycle with Direct-fired Heat, *Ref. Nat. Gaso. Mfr.*, June, 1937, p. 305.

VAIDEN, J. W.: Economics of Liquefied Pet. Gases, *Oil Gas J.*, May 23, 1940, p. 74.

CHAPTER XXVI

CHEMICAL AND CLAY TREATMENT

With few exceptions all petroleum products must be chemically treated in some manner in producing finished market products. The impurities that must be removed are usually present in the crude oil, but some are also produced during the refining operations of distillation, cracking, etc. Some of the purposes of chemical treatment are as follows:

1. To improve the color.
2. To remove sulfur.
3. To improve the odor.
4. To remove gumlike, resinous, and asphaltic substances.
5. To improve the stability upon exposure to air or light.
6. To eliminate corrosive materials.
7. To change properties of the oil, such as the Viscosity Index, carbon residue, etc.
8. To produce a more salable and desirable market product.

Most stocks do not need to be improved in all of these respects, but some stocks, such as pressure-still distillate that is produced from sulfur-bearing crude oil, must be treated for many of the aforementioned purposes.

Although many chemicals are used for refining, *sulfuric acid* has in the past been the most useful and generally used chemical. Sulfuric acid treatment improves the color, removes sulfur, reduces the gum content, improves the stability of light distillates, and to some extent improves the odor. It is also used to improve the color of lubricating oils and sometimes wax. For "sour" sulfur-bearing light distillates, the *doctor treatment* must be used. This treatment consists of agitating the oil with a little sulfur and an alkaline solution of sodium plumbite. The odoriferous mercaptans, hydrogen sulfide and elementary sulfur, are removed or converted into less harmful forms. A newer treatment for somewhat the same purpose is the *hypochlorite process,* in which the oil is agitated with an alkaline solution of sodium or calcium hypochlorite. Solutions of *sodium hydroxide* are generally used after acid treatment to neutralize the excess acid and to remove sulfonic acids and other organic acids, as the sodium salts. Used alone, it removes hydrogen sulfide and to some extent the mercaptans or thioalcohols. Sodium hydroxide, when used to neutralize acid-treated lubricating oils, often gives troublesome emulsions, and hence *neutralizing clays* and *ammonia* are being more widely used for this purpose. The color of lubricating oils is improved by percolation through adsorbent clays or by contacting the oil, after acid treatment, with clay at a high temperature. In addition to these, there are many other processes such as the clay vapor-phase processes for cracked gasoline; the Solutizer, copper chloride, and catalytic desulfurization treatments for light distillates; and the Edeleanu solvent process. Since 1933 there has been a widespread development of *solvent treating* or *extraction* processes. In general, these processes aim to separate the high- and low-viscosity-index lubricating oil hydrocarbons by selective absorption. These will be discussed in Chap. XXVII.

SULFURIC ACID TREATMENT

Sulfuric acid has been used since the first days of the oil industry, and even before that, for treating coal oil. No single substitute for acid has been found, but a number of new methods have been encroaching on the use of acid.

The action of sulfuric acid on the several series of hydrocarbons is different for each series. The paraffins and naphthenes are only slightly attacked by 93 per cent acid (66 Bé.) at room temperature. At higher temperatures and at higher concentrations of acid they are attacked, and particularly those isomers which have several side-chains. Inasmuch as straight-run gasolines are composed largely of paraffin and naphthene hydrocarbons, sulfuric acid is an excellent treating agent for them if any treatment is necessary. The aromatic hydrocarbons, such as benzene and its homologues, are only slightly attacked by 93 per cent acid but toluene and xylene are more readily attacked than benzene. The aromatic hydrocarbons cause lamp oils to burn with a smoky flame. For the removal of aromatics, 93 per cent and higher strengths of acid are useful and sometimes even fuming acid is necessary. Liquid sulfur dioxide is even more suitable for extracting aromatics.

The unsaturated hydrocarbons, such as the olefins, diolefins, and acetylenes, are readily attacked by sulfuric acid even at strengths as low as 75 per cent. The olefins tend to polymerize to di- or higher polymers, some of which[1] are highly resistant to further action by the acid. Cracked gasoline contains olefins in considerable quantity, and their polymerization may account in part for the increase in end-point during acid treatment. High temperatures and high concentrations of acid favor polymerization, and low temperatures and low concentrations favor the formation of alkyl acid sulfates, neutral esters, and secondary and tertiary alcohols. The higher alcohols and dipolymers and to some extent the acid alkyl sulfates dissolve in the distillate, and upon redistillation the acid alkyl sulfates decompose, yielding alcohols, sulfur dioxide, etc., and cause trouble with the color, stability, and gum content of the gasoline. The acid alkyl sulfates are dissolved by a caustic wash, after acid treatment, but the neutral esters are not, and at temperatures above 285°F. they decompose. Diolefins cause the formation of tars, a loss in color, and the formation of "gum" during storage.[1]

Sulfuric acid also removes resinous or asphaltic substances that may be present due to poor fractionation, entrainment, or a small amount of cracking. These materials tend to inhibit the crystallization of wax, and hence acid treatment often raises the pour-point. Oxygen compounds, such as naphthenic acids and ketones, and substances such as alcohols and aldehydes that are formed by high-temperature oxidation are dissolved by sulfuric acid, but when diluted with oil their removal is never complete. Nitrogen bases similar to quinoline or pyridine, which are produced in small quantities during distillation, are easily dissolved in dilute acid.

Many sulfur compounds are present in petroleum, but not many of them have been isolated or studied. The action on mercaptans will serve as an illustration of the action of acid:

$$\begin{aligned} RSH + H_2SO_4 &= RS\text{—}SO_3H + H_2O \\ RSH + RS\text{—}SO_3H &= (RS)_2SO_2 + H_2O \\ (RS)_2SO_2 &= R_2S_2 + SO_2 \end{aligned}$$

The final disulfide products are partly dissolved in the acid sludge. Strong acid (93 per cent or stronger) is necessary to remove mercaptans, but such large quantities of acid are required that "sweetening" is seldom practiced in this manner. Alkyl sulfides, disulfides and sulfates, and most sulfur compounds are removed by 93 per cent or stronger acid, but the acid alkyl sulfates dissolve to some extent in the oil.

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[1] BROOKS and HUMPHREY, *J. Am. Chem. Soc.*, **40**, 822 (1918).

The rate[2] of action of sulfuric acid on the various impurities appears to be somewhat as follows: (1) nitrogen compounds such as amines, amides, and amino acids; (2) asphaltic substances; (3) olefins; (4) aromatics; and (5) naphthenic acids.

The loss in octane number of gasoline is not large for normal quantities of acid. Born and Wilson[3] have studied three pressure distillates by treating under conditions comparable to those used in the respective plants from which the distillates were obtained. Table 91 gives their results. Wirth, Kanhofer, and Murphy[4] present similar data except that the total loss in octane number was divided into the loss due to (1) evaporation and loss of light hydrocarbons during steam distillation, (2) polymerization and solution during treatment, and (3) heavy hydrocarbons remaining as a residue upon distillation. The first of these gave losses in the octane number of 0 to 2; the second gave losses of 1 to 2.5; and the third was negative, or the octane number increased by 0 to 1 owing to the elimination of heavy ends. Their results are comparable with those given in Table 91.

TABLE 91.—EFFECT OF ACID TREATMENT ON OCTANE NUMBER

Lb. acid per bbl.	Octane Nos.* for				
	Distillate *A*		Distillate *B*		Distillate *C*
	66°Bé.	62.5°Bé.	66°Bé.	62.5°Bé.	66°Bé.
0	70.0	70.0	68.5	68.5	67.4
1	68.9	69.0	67.3	67.4	66.1
2	68.2	68.3	66.6	66.8	65.7
3	67.7	67.8	66.2	66.4	65.1
5	67.1	67.3	65.8	65.9	64.7

* 30-B Ethyl engine, 212°F. jacket temperature, 15-deg. spark advance.

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[2] PYHÄLÄ, E., *Petroleum*, **9**, 1506 (1928).

[3] *Nat. Petroleum News*, Apr. 5, 1933, p. 23.

[4] Control of Color . . . Treating, *Ref. Nat. Gaso. Mfr.*, December, 1930, p. 89.

Concentration of Acid.—Sixty-six Baumé[1] or 93 per cent acid finds the most general use. However, for treating light distillates to color only, a more dilute acid may be advantageous.[5] For most other purposes, such as removing combined sulfur, improving the burning qualities of kerosene, and removing tar from lubricating oils, a 93 per cent or stronger acid should be used. For lubricating oil, 98 per cent acid is also widely used.

The loss of oil to sludge increases as high concentrations of acid are used so that in general the most dilute acid that is suitable should be used. The following data by Potthoff[6] indicate for pressure distillate the larger sludge loss and the total loss (sludge and polymerization) that occur by using strong acid:

Lb. acid per bbl.	Sludge loss		Total loss	
	66° acid	60° acid	66° acid	60° acid
5	1.8	1.6	2.8	2.2
10	3.5	2.7	5.3	3.9
20	8.0	4.7	11.3	6.3

Weir, Houghton, and Majewski[7] have conducted experiments with a light lubricating oil stock (289 viscosity at 100°F.) that show the following effect of acid strength:

Lb. acid per bbl.	Sludge loss with these strengths of acid			
	75%	86%	93%	98%
6.25	0.7	0.92	1.75	2.35
12.5	1.1	1.6	2.3	3.1
31.3	1.3	1.95	3.1	4.15

Thus with small amounts of acid, such as those customarily used in treating distillates, the sludge losses are small; and although the loss increases with the strength of acid, it is of such a magnitude that the effect of acid concentration may be almost neglected. However, for quantities of acid exceeding 10 lb. per barrel, the loss caused by using strong acid begins to be important. The exact strength that should be used depends entirely upon the impurities that must be removed, the types of hydrocarbons found in the oil, and the final color that is desired. Strong acid (93 to 103 per cent), when used at relatively low temperatures, is effective in removing combined sulfur and aromatic hydrocarbons from burning-oils (and transformer oils), but in general the color of the product, when fuming acid is used, is not good because oxidation of some of the less stable compounds occurs.

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[5] KALICHEVSKY and STAGNER, "Chemical Refining of Petroleum," p. 51, Chemical Catalog Company, Inc., New York, 1933.

[6] Purification of Pressure Distillate, *Oil Gas J.*, Mar. 5, 1931, p. 141.

[7] Control of Color . . . Treating, *Ref. Nat. Gaso. Mfr.*, December, 1930, p. 89.

Cooke and Hayford[8] report the following effect of acid strength on the removal of sulfur from pressure distillate by the Stratford contactor centrifuge process.

Strength of Acid, Per Cent	Per Cent Sulfur in Treated Distillate
80	0.2
93	0.17
95	0.13
98	0.09
100	0.075
104	0.07

For improvement of color, an acid of 93 per cent strength is recommended; but if the combined sulfur is low, an acid of only 85 per cent strength may be advantageous. Weak acid is also useful in removing nitrogen bases and for improving the color without removing unsaturated compounds. The concentration of acid that is most suitable for a particular stock can be ascertained only by laboratory and plant-scale experiments.

Quantity of Acid.—Enough acid must be used to improve the color and remove impurities, but an excess over this amount may result in a poorer color and a loss of aromatic and unsaturated hydrocarbons as well as a waste of acid. If acid is applied to lubricating oils in too large doses, the oil may be discolored by "burning." The remedy is to use the acid in small charges and keep the oil cool. The treatment of spray oils, medicinal oils, and sometimes wax is accomplished by adding fuming acid in

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[8] Distillate Treating, Part II, *Ref. Nat. Gaso. Mfr.*, April, 1934, p. 130.

25 or 30 lb. per barrel charges and using as much, in some cases, as 200 lb. of acid per barrel.

The quantity of acid that is commonly used is about as follows:

Natural gasoline—Usually none but occasionally 2 lb. per barrel.
Straight-run gasoline—Usually none but may require 5 lb. per barrel for sulfur removal.
Pressure distillate—To improve the color, normally 1 to 4 lb. per barrel. For high-sulfur oils and oils from naphthene-base crude oils the quantity may be much more. Some distillates cannot be economically desulfurized with acid.
Solvents—0 to 5 lb. per barrel. High-sulfur stocks are seldom used in solvent manufacture.
Kerosene—1 to 15 lb. but as much as 75 lb. per barrel for the kerosene from some naphthene-base crude oils.
Lubricating oils—0 to 60 lb. per barrel. Pennsylvanian oils usually require no acid treatment; mixed-base oils more; and asphalt-base oils the higher figure. Vacuum-distilled stocks require less acid than residual stocks. The acid required for lubricating oils is intimately connected with the amount of percolation or contacting that is practiced.

Cooke and Hayford[8] find that the desulfurization is directly proportional to the amount of acid that is used.

Amount of Acid, 98 Per Cent, Lb. per Bbl.	Per Cent Sulfur in Treated Distillate
5	0.165
8	0.142
11	0.117
14	0.095

Temperature of Treatment.—The temperature at which the treatment is conducted is one of the most important factors. Although the temperature for a particular stock should be determined by experiment, the following considerations are useful as a guide:

Polymerization losses are greater at higher temperatures, so that unless polymerization is desired, as in rare cases when the sludge is to be utilized, lower temperatures are desirable.

High temperatures favor the removal of aromatic and unsaturated hydrocarbons and of resinous asphaltic materials. Thus naphthenic kerosenes and solvents are usually refined at a relatively high temperature unless the removal of sulfur is also necessary.

Lower temperatures produce a better color in the product and are favorable for the removal of sulfur compounds. Sludge losses are slightly higher at lower temperatures; but as the quantity of acid that is required is also less, the actual sludge loss is not greatly affected. In treating lubricating oils at low temperatures the viscosity of the oil may be so great that settling is slow and the separation is imperfect. This results in too long a contact time and a loss in color, and hence lubricating oils are usually treated at relatively high temperatures. Table 92 illustrates the effect of temperature on color when a kerosene stock is treated with 17.5 lb. of acid per barrel (99 per cent acid).[9]

TABLE 92.—EFFECT OF TEMPERATURE ON COLOR

Temperature, deg. F.	Acid sludge, g. per l.	Arbitrary color scale, mm.
32	61.6	193.0
41	62.0	166.5
50	62.5	143.0
59	63.5	112.5
68	64.3	89.5
77	64.8	80.5
86	65.2	52.0
95	65.8	Yellow
104	66.0	Yellow
113	66.4	Yellow
122	67.0	Yellow

The effect of the temperature of treating upon sulfur removal[5] is illustrated by Table 93. The cracked-gasoline stock contained 0.39 per cent sulfur, and 90 per cent of the treated material was distilled with steam.

The temperatures that are commonly used for various treating operations are as follows:

Straight-run gasoline—70 to 90°F. If large quantities of acid are required, it may be practical to go to lower temperatures.

Cracked gasoline—60 to 90°F. If heavy treats are required, temperatures of 25 to 30°F. are recommended, although temperatures of 40 to 50° may be more economical[10] (Table 93).

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[9] ZALOZIECKI, R., *Chem. Ztg.*, 875, 1895.

[10] Standard Oil of California, Brazilian Pat. 5,667 (Jan. 23, 1929) and other patents.

Kerosene—90 to 130°F. If the oil is to be redistilled, a higher temperature may be economical. Robinson[11] finds that low temperatures are better.

TABLE 93.—EFFECT OF TEMPERATURE ON SULFUR REMOVAL*

Acid strength, per cent H_2SO_4	Treating temp., deg. F.		H_2SO_4, net lb. per bbl.	Loss to sludge, per cent	Engler dist. of neutral oil to 400°F., per cent	Sulfur in steam dist., per cent
	Initial	Max.				
103	88	98	10	5.2	90.5	0.26
103	80	98	20	6.7	88.0	0.19
103	86	102	30	10.0	....	0.16
103	80	104	40	12.0	....	0.14
103	74	106	60	16.0	80.3	0.10
103	7	20	10	5.2	92.0	0.32
103	2	20	15	6.0	91.5	0.17
103	7	23	20	9.0	88.0	0.10
103	2	25	30	10.4	87.0	0.06
93	93	102	10	4.2	91.5	0.25
93	84	97	20	5.8	88.5	0.21
93	78	96	30	8.3	....	0.16
93	76	101	40	13.3	....	0.14
93	84	102	60	16.7	81.5	0.10
93	10	16	10	4.2	93.5	0.34
93	8	18	20	5.8	92.5	0.25
93	5	20	30	10.0	91.0	0.12
93	0	21	40	10.8	90.0	0.07
93	5	28	60	15.8	....	0.04

* Courtesy of Union Oil Company of California.

Lubricating oil stocks—Customary temperatures[12] are given in Table 94.

Cylinder stock—130 to 170°F.[12] and 150 to 180°F. if treating is conducted before dewaxing.

The cold-treating methods have many advantages from a treating standpoint, but the refrigeration requirements are enormous. The practicability of low-temperature treating must be carefully investigated and a stock must be very difficult to treat before cold methods can be adopted.

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[11] ROBINSON, C. L., U.S. Pat. 910,584 (Jan. 26, 1909).

[12] KAUFFMAN, H. L., *Ref. Nat. Gaso. Mfr.*, May, 1927, p. 59.

TABLE 94.—TEMPERATURE FOR TREATING LUBRICATING OILS

Viscosity of oil at 100°F., sec.	Temperature of oil when acid is added, deg. F.	Temperature of oil and wash water during washing and settling, deg. F.
50	70– 80	110–120
75	80– 90	120–130
100	85– 95	130–140
150	90–100	140–150
200	95–105	150–160
300	100–110	155–165
500	105–115	160–170
1,000	110–120	165–175
1,500	110–120	165–175
2,000	115–125	170–180

Contact Time.—Two factors are involved in considering the contact time. Prolonged contact of acid-sludge and oil results in a poorer color and less stability, but too short a time may prevent a complete utilization of the acid. Furthermore, the time of contact is intimately associated with the fineness of dispersion of the acid throughout the oil and the time required to separate the sludge.

Straight-run and cracked gasolines are contacted with acid for less than a minute in continuous-treating systems. A short contact time is particularly advantageous for cracked gasolines in order to minimize polymerization and sulfation of the oil. The time of contact is sometimes held to only a few seconds by mechanical contactors,[13] and the settling time is eliminated almost altogether by centrifugal means. Continuous processes for treating lubricating oils are being investigated,[14,15,16] and a short time of contact (10 min.) is found to be advantageous. These short-contact processes all claim to reduce the amount of acid that is required and to facilitate the control of the treating operation.

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[13] STRATFORD, C. W., *Nat. Petroleum News*, Mar. 12, 1930, p. 32F.

[14] JONES, L. D., Use of Centrifuge in Acid Treating Petroleum Stocks, *Ref. Nat. Gaso. Mfr.*, June, 1934, p. 224.

[15] WALKER, R. C., Continuous . . . Centrifugal Separation . . . , *Ref. Nat. Gaso. Mfr.*, June, 1934, p. 228.

[16] TRESCOTT, L. C., Sludge, *Ref. Nat. Gaso. Mfr.*, May, 1934, p. 172.

In the older method of batch agitation, the time of contact is much longer. For light distillates the time of air agitation ranges from 15 to 40 min. Kerosene normally requires 30 or 40 min., and for lubricating oils the time may be 90 min. The time required to settle the sludge in an agitator ranges from a few minutes for gasoline to as long as 15 hr. for very viscous stocks.

Laboratory control tests are necessary in finding the best conditions for treating. An excellent method for the control of lubricating oil treating is outlined by Weir, Houghton, and Majewski.[7]

Inhibitors of Gum.—During cracking, unsaturated hydrocarbons are produced that upon exposure to air during storage produce so-called gum in the gasoline. Gum may be removed by treatment with sulfuric acid or by vapor-phase treatment with fuller's earth, but the use of antioxidants or inhibitors is becoming more and more common because of the small expense of such a treatment. Inhibitors delay the formation of gum; but if sufficient time elapses, they do not prevent its formation. Exposure to sunlight, elevated storage temperatures, or a high percentage of sulfur contributes[17] to more rapid gum formation. The stability of gasoline may be taken as proportional to the induction period in oxidation bomb tests for gum. Thus the amount of gum by the A.S.T.M. method is a direct function of time for each temperature,[18] and the length of time for the formation of, say, 10 mg. of gum during storage can be estimated by extrapolation of laboratory tests.

Among inhibitor agents are such synthetic materials as dibenzyl-para-aminophenol, monobenzyl-para-aminophenol, para-hydroxyphenylmorpholine, tributylamine, alpha-naphthol, and catechol; in coal-tar distillates, cresols and xylenols; and in wood-tar distillates, creosote, catechol, ethyl guaiacol, mono ethers of pyrogallol, and the xylenols.[19] The amount of each inhibitor required varies widely, but to some extent this is counteracted by a cost that is inversely proportional to effectiveness. Minute amounts of heavy metals such as copper or vanadium act as catalysts in producing gum, and certain compounds have been developed for counteracting[20] this effect.

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[17] McNamara, . . . Gum Stabilities of Gasoline, *Ref. Nat. Gaso. Mfr.*, October, 1934, p. 381.

[18] Yabroff and Walters, Gum Formation in Cracked Gasolines, *Ind. Eng. Chem.*, **32**, 83 (1940).

Inhibitors for color deterioration have also been proposed, and the use of dyes for counteracting or masking the true color is common.

SWEETENING TREATMENTS

Mercaptans and elementary sulfur are not removed from distillates by the ordinary treating processes. The so-called sweetening treatments are used to eliminate the effect of these substances. Mercaptans impart a foul odor to the distillate, and elementary sulfur (in the presence of mercaptans) causes the distillate to be corrosive. Hydrogen sulfide is also removed in the doctor treatment, or it may be removed by a caustic wash. The common sweetening processes are the doctor, the hypochlorite, the copper chloride, and several alkali wash treatments. Indirectly, mercaptans and sulfur compounds decrease the octane number of gasoline and its susceptibility to the action of tetraethyl lead. Thus, sweetening methods that remove sulfur rather than convert it into other forms are most satisfactory. This fact is a main argument for the alkali wash and the Solutizer processes. The color stability of some gasolines is also closely related to sulfur content, to the methods of conducting sweetening, and to certain mechanical separations of refining.[21]

Caustic washing methods, which involve bringing the gasoline in contact with sodium,[22] calcium,[23] or magnesium (brucite) hydroxides for the removal of hydrogen sulfide and mercaptans, are feasible for some gasolines because of the improvement in lead susceptibility and the saving in chemicals in subsequent treatments. Caustic solutions ranging from 5 to 15 per cent are employed.

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[19] ROGERS and VOORHEES, Gum Formation in Gasoline II, *Ind. Eng. Chem.*, **25**, 520 (1933).

[20] DOWNING, CLARKSON, and PEDERSEN, . . . Metal Catalysts in Gaso. Gum Formation, *Oil Gas J.*, July 27, 1939, p. 97.

[21] BERGER, C. W., Practical Aspects of Sun Stability, *Ref. Nat. Gaso. Mfr.*, **15**, 411 (1936).

[22] RIDGWAY, C. M., Improving Gasoline by Caustic Washing, *Oil Gas J.*, Mar. 31, 1938, p. 83.

[23] ANON., Lime Wash . . . Sulfide Removal, *Ref. Nat. Gaso. Mfr.*, April, 1940, p. 81.

D. L. Yabroff *et al.*[24] developed the *Solutizer* process, which permits complete removal of mercaptans by a caustic solution to which has been added an organic agent that increases the solubility of mercaptans in the caustic solution. Among suitable solutizers are various mixtures of the hydroxide, isobutyrate, alkyl-phenolate, and carbonate salts of sodium or potassium. The low-molecular-weight mercaptans are dissolved by caustic alone, but solutizers must be added in order to remove the mercaptans having three or more carbon atoms to the molecule. The spent solution is freed from mercaptans by stripping with steam and can then be used again.

Although bauxite desulfurization differs vitally from what have been termed sweetening processes, it serves the same purpose and in addition is able to remove more stable sulfur compounds than those involved in sweetening. In this process the oil is heated to 700 to 800°F. and contacted with bauxite. The sulfur is reduced to extremely low percentages.

The *doctor treatment* consists of agitating the oil with a little sulfur and with alkaline sodium plumbite solution. Reactions for the process are as follows:

$$2RSH + Na_2PbO_2 = (RS)_2Pb + 2NaOH$$
$$(RS)_2Pb + S = R_2S_2 + PbS$$

Most of the lead sulfide settles, but the disulfides dissolve in the oil to some extent. Inasmuch as disulfides decompose at elevated temperatures,[25] the doctor treatment should preferably be conducted after the final distillation of cracked distillates. Elementary sulfur in the gasoline is removed by these reactions; but if an excess (about 20 per cent more than required for the reaction) of sulfur remains in the oil, the oil will be corrosive. The presence of lead sulfide facilitates the sweetening process, and oxygen is also advantageous.[26] Hence air agitation is an advantage in doctor sweetening. The doctor treatment is always difficult to control, and hence the chemistry of the process must be considered for each particular distillate.[26] Gasolines that contain much free sulfur sometimes require the addition of mercaptans or sour distillates before the doctor treatment, because mercaptans are necessary in completing the reactions with sulfur. Stability of color is greatly improved by thorough separation of chemicals during settling and washing.

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[24] The Solutizer Process, *Ref. Nat. Gaso. Mfr.*, May, 1939, p. 171; The Regeneration Step . . . , *Ref. Nat. Gaso. Mfr.*, November, 1939, p. 131; and . . . Octane Number and Lead Susceptibility . . . , *Ref. Nat. Gaso. Mfr.*, March, 1940, p. 55.

[25] Excepting ethyl and propyl disulfides. Faragher, Morrell, and Comay, *Ind. Eng. Chem.*, **20**, 527 (1928).

The concentration of the sodium hydroxide solution should be 12 to 30°Bé. (8 to 24 per cent). Lead oxide or litharge (PbO) is dissolved in the caustic solution before it is mixed with the oil. The solubility of lead oxide in caustic soda increases with the gravity of the solution, being about 1 per cent in a 12°Bé. solution and about 3 per cent in a 30°Bé. solution. About 0.05 lb. of lead oxide is consumed per barrel of cracked gasoline. Rhombic or lump sulfur should be used because flowers of sulfur is not sufficiently soluble in oil. Continuous-treating equipments are generally used, but batch treatment with air agitation has the advantage of regenerating the lead sulfide and decreasing the amount of sulfur that is required. Sometimes a better color gasoline is obtained by using the caustic solution from a hydrogen sulfide wash in making the doctor solution.[27]

Spent doctor solution is often recovered or used over again by adding more litharge to the solution and carrying the sulfide in suspension. Some refiners oxidize the lead sulfide as a caustic slurry by heating to 150 to 175°F. and blowing with air, which converts the sulfide to plumbite.[28] Doctor solution may also be recovered by the use of chlorine or sulfuric acid.

Lead sulfide itself may be used as a sweetening agent. The over-all reaction is the same as those given for doctor sweetening, but the lead sulfide may act catalytically to cause the two doctor reactions to take place simultaneously as

$$2RSH + S + 2NaOH \rightarrow R_2S_2 + Na_2S + 2H_2O$$

The reaction may be conducted by contacting the sour gasoline, sulfur, and oxygen (air) wth a solid bed of lead sulfide catalyst[29] or by recycling the lead sulfide suspended in a strong caustic solution[30] with the introduction of air and current revivification of part of the lead sulfide solution by washing with hot water.

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[26] Born, S., Chemical Reactions . . . , *Petroleum Eng.*, August, 1931, p. 149.

[27] Rowsy and Whitehurst, *Oil Gas J.*, Dec. 29, 1927, p. 250.

[28] *Chem. Met. Eng.*, **38**, 76 (1931); also D. F. Gerstenberger, *Petroleum Eng.*, January, 1930, p. 167.

Sodium or calcium *hypochlorite sweetening* has found extensive use in the treating of natural gasoline and straight-run gasoline, but it is seldom used for cracked products or high-boiling oils. With dilute hypochlorite a mild oxidation takes place thus:

$$2RSH + NaOCl = R_2S_2 + H_2O + NaCl$$

With more concentrated solutions

$$RSH + 3NaOCl = RSO_3H + 3NaCl$$

Likewise for sulfides

$$R_2S + NaOCl = R_2SO + NaCl$$

and

$$R_2S + 2NaOCl = R_2SO_2 + 2NaCl$$

Elementary sulfur is not attacked, and hydrogen sulfide is partially oxidized to water and free sulfur. The sulfones (R_2SO_2), such as ethyl and propyl sulfones, can be removed by washing with water, but the higher molecular-weight sulfones are not soluble in water.

Sodium hypochlorite is commonly prepared by bubbling chlorine gas through a 10 per cent solution of sodium hydroxide. The temperature should not be over 95°F., or chlorates may be produced. A water-cooled cast-iron vessel may be used, but steel is satisfactory. The stock solution is diluted to about 0.34 *N* when ready to use. The quantity of solution required, measured in terms of chlorine, amounts to 1 to 15 lb. of chlorine per thousand gallons.

Calcium hypochlorite is more convenient to use and is somewhat cheaper than sodium hypochlorite. The solution may be prepared as above, with lime and chlorine, but bleaching powder is often more convenient. A 0.34 *N* solution is satisfactory. The Mathieson Alkali Works has a special chlorinated calcium compound sold as H.T.H. [$Ca(OCl)_2$] which contains about 65 per cent chlorine. The quantity of H.T.H. required is usually between 1 and 5 lb. per thousand gallons of gasoline, and three to five times as many pounds of a good grade of bleaching powder ($CaOCl_2$) is required.

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[29] HAPPEL and ROBERTSON, Lead Sulfide . . . Dry Sweetening Agent, *Oil Gas J.*, Mar. 31, 1938, p. 125.

[30] ALTSHULER and GRAVES, Refinements in Sweetening Technique, *Ref. Nat. Gaso. Mfr.*, June, 1937, p. 272.

The hypochlorite process partially oxidizes hydrogen sulfide to free sulfur, so that a precaustic wash is sometimes used to remove hydrogen sulfide. In fact, a caustic wash materially reduces the chemical that is needed in the hypochlorite treat. Little or no sludge is produced so that the process is particularly suited to the processing of natural gasoline.

The *copper sweetening* process involves the oxidation of mercaptans to disulfides and the reduction of cupric chloride to the cuprous state, as

$$4RSH + 4CuCl_2 \rightarrow 2R_2S_2 + 4CuCl + 4HCl$$

The cuprous chloride is then oxidized with air or oxygen:

$$4CuCl + 4HCl + O_2 \rightarrow 4CuCl_2 + 2H_2O$$

In the solid process both reactions take place simultaneously in a vessel packed with fuller's earth impregnated with cupric chloride. For oxygen-sensitive stocks, however, such as certain cracked gasolines, the oxidation must not be conducted in the presence of the gasoline, and hence a liquid solution process is employed in which the air is admitted to the solution in a separate vessel.[31] Hydrogen sulfide and lower mercaptans are removed in a preliminary caustic wash. In the solution process the use of somewhat expensive glass-lined, rubber-lined, Durichlor, concrete, and canvas-base Bakelite equipment is necessary for withstanding the violent corrosive action of cupric chloride and hydrochloric acid.

REFINING BY ADSORPTION

Various mineral clays, earths, and artificial mineral adsorbents are used to improve the color of oils and remove asphaltic or resinous material. In general, three methods are followed: (1) percolation through a long column of coarse clay, (2) contact at a high temperature with finely powdered clay, and (3) contact in the vapor-phase with loosely packed clay. The percolation method is the oldest method and in many ways is not so satisfactory as contact treatment, but in other ways, particularly its flexibility, it is a desirable method. The application of vapor-phase treating is limited to the treatment of the lighter distillates, particularly cracked gasoline, because higher boiling oils cannot be easily kept in the vapor state. The contact process is now used for neutral oils, gasoline, and diluted cylinder stocks.

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[31] SCHULZE and BUELL, Control of Copper Sweetening . . . , *Oil Gas J.*, Nov. 25, 1937, p. 56.

The removal of coloring matter from oils by clay appears to be governed by the adsorption isotherm of Freundlich.[32] This may be stated as

$$\frac{X}{M} = aC^{\frac{1}{n}}$$

or in logarithmic form

$$\log \frac{X}{M} = \log a + \frac{1}{n} \log C$$

where X = units of impurity removed.
M = quantity of adsorbent used.
C = concentration of the impurities in the oil or vapor, in equilibrium with the solid adsorbent.
a and n = constants that depend upon the characteristics of the adsorbent, oil or vapor, and solvent if one is used.

Thus decolorizing data yield straight lines if X/M is plotted against C on logarithmic graph paper. The equation may be used to compare several clays, but this is about the limit of its usefulness, because the value of the constants is usually unknown. L. L. Davis[33] presents a study of five clays in the treatment of a lubricating oil. He found the reciprocal of the Tag Robinson color was a satisfactory measure of the impurities. For comparing the efficiency of two clays on a particular oil, the foregoing equation may be arranged in a more convenient form by dividing one equation by the other, thus

$$\frac{M}{M'} = \frac{a'}{a} C^{\left(\frac{1}{n'} - \frac{1}{n}\right)} \quad \text{or} \quad bC^{\left(\frac{1}{n'} - \frac{1}{n}\right)}$$

Table 95 shows the efficiencies of the five clays.[33]

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[32] WALKER, LEWIS, MCADAMS, and GILLILAND, "Principles of Chemical Engineering," 3d ed., McGraw-Hill Book Company, Inc., New York, 1937.

[33] *Ref. Nat. Gaso. Mfr.*, March, 1928, p. 90.

TABLE 95.—COMPARISON OF CLAYS

Tag Robinson color	Efficiencies as per cent of Riverside earth				
	Riverside, Tex., fuller's earth	Natural, Utah	Treated German clay, dry form	Treated Tex. clay, pulp form	Treated Calif. clay, pulp form
½	100	120	120	170	285
1	100	130	133	235	400
1½	100	140	140	240	465
2	100	150	150	245	500

Many factors are involved in the efficiency of decolorizing, such as the kind of oil; the kind of treatment that it has undergone; the kind of solvent, if any is used; and the presence of sludge or tarry material; and hence, a fair cataloguing of clays in the order of efficiency cannot be made. In the selection of a clay, examinations of the clays that are available in the vicinity should be made in the laboratory. As an indication of the difference in clays note Table 96 by Dunstan.[34] He examined the decolorizing power of the adsorbents using a 0.25 per cent solution of crude asphaltic oil in benzene.

TABLE 96.—COMPARISON OF DECOLORIZING MATERIALS

Material	Cc. of colored solution decolorized by 1 g. of clay	Approximate bbl. per ton
Alumina	60	342
Fuller's earth I	30	171
Bauxite I	30	171
Bauxite II	25	142
Bauxite III	20	114
Ignited peat	15	85
Bone charcoal	14	80
Bog iron ore	12	68
Fuller's earth II	10	57
Ferric oxide	10	57
Ball clay	8	45
Fuller's earth III	8.5	47
Fuller's earth IV	4	23
China clay	2	11.5
Kieselguhr	2	11.5

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[34] MORRELL and EGLOFF, reference, *Oil Gas J.*, Jan. 28, 1932, p. 22.

The more important groups of adsorbents are (1) fuller's earth, (2) bentonite, (3) various clays, (4) bog iron ore, and (5) bauxite and alumina. These are often sold under trade names such as "Palex," "Filtrol," "Floridin," and "Kontak." The chief sources of bleaching clays in the United States are Georgia, Florida, southern Illinois, Texas, Colorado, Utah, Nevada, Arizona, and southern California, although suitable clays are found in many other states.[35] Some are used in the natural state, except for drying and crushing, but others are burned and washed with water, steam, hydrochloric, or sulfuric acid. The treated clays usually have a greater decolorizing power, but the treatment is expensive. Most clays can be reactivated by burning, and some by washing with solvents.

In general, the hydrocarbons are adsorbed in the following order: unsaturates, aromatics, naphthenes, and paraffins. In each series the high-molecular-weight hydrocarbons are adsorbed more readily, and this doubtless accounts for most of the decolorizing action. Thus the specific gravity, viscosity, and color of the stream of oil from a percolation filter increase as more and more oil flows through the filter, and the first oil will be of a much lower gravity and viscosity[36] than the parent stock. Resinous and asphaltic substances are actively adsorbed. Little of the sulfur is adsorbed, and hence clay-treating methods are seldom used for desulfurization.

TREATING EQUIPMENT

The mechanical operations involved in treating are primarily those of mixing or contacting and settling or separating. In the most simple arrangement, a *batch system*, which employs a so-called *agitator*, may be used. The system consists of a conical-bottom agitator vessel equipped with a steam coil and having connections for agitation with air or for circulation by means of pumps. A single agitator may be used for many operations such as contact with sulfuric acid or alkalies, washing with water, or neutralization with ammonia or clay. A lead lining weighing 8 to 10 lb. per square foot is usually provided. Lead is a ductile material, and hence it should be supported at intervals of about 8 in. by reinforcing bars. The support bars are bolted through the lead to the steel shell, and a strip of lead is burned over each bar and its bolts, so that no steel is exposed. Hard lead (94 Pb-6Sb) and tellurium lead are gaining in favor because of their greater strength.

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[35] NUTTING, P. G., *Ind. Eng. Chem., Anal. Ed.*, **4**, 139 (1932).

[36] KAUFFMAN, H. L., *Ref. Nat. Gaso. Mfr.*, April, 1928, p. 74.

Continuous treaters involve many arrangements of mixers and settlers, but in principle they are much alike. The most simple arrangement is a metering and mixing system such as would be employed in adding tetraethyl fluid or inhibitors to gasoline or demulsifying agents to crude oil. Although injection can be controlled by hand, the best methods employ proportioning pumps actuated by the main transfer pump, proportioning orifice flow controllers, or similar automatic proportioning methods. Such systems are illustrated in Fig. 173 for introducing an inhibitor into gasoline. If extremely small amounts of agent are added, as in the case of ethyl fluid or by the hand-control method of Fig. 173, a more uniform mixture may be attained by recirculating it in and out of the final storage tank.

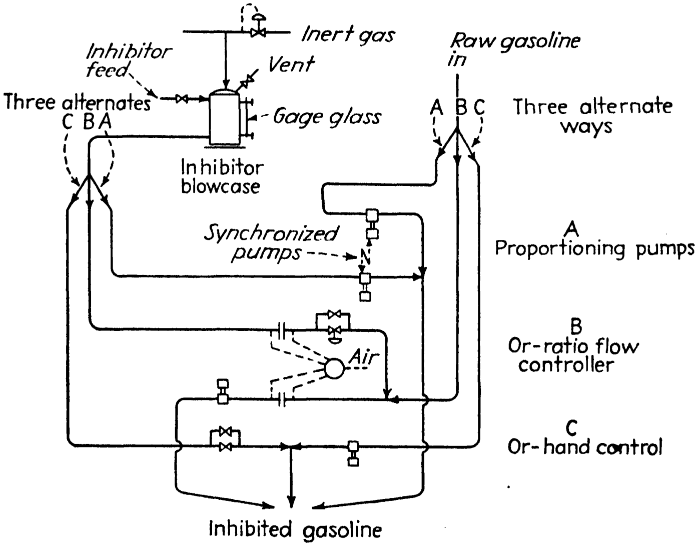

FIG. 173.—Three methods of adding inhibitor to gasoline.

A somewhat different system is necessary for contacting a fluid with a solid treating agent, as in passing gasoline and air through a copper chloride solid treating agent or in adding sulfur to gasoline in the doctor sweetening process. Such equipment is so simple that no flow diagram will be shown. When contacting a liquid reagent with the stock, it is necessary to have some method of recirculation and perhaps of mixing the two fluids and an additional vessel for settling traces of the treating agent or for washing with water. Such systems are illustrated by the caustic-wash system of Fig. 174.

Many modifications and elaborations on these systems are possible, such as the use of motor-driven contactors for mixing the stocks, centrifuges for separating the stocks, filters for removing traces of solids, and various sequences of contacting, settling, washing, etc., as illustrated in the pressure-distillate treater of Fig. 177 (page 599).

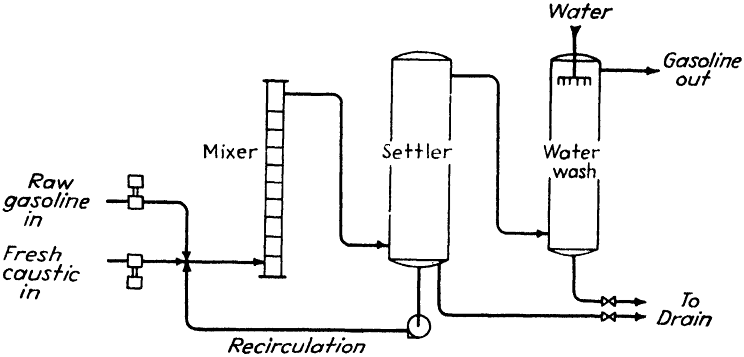

FIG. 174.—Caustic-wash system with recirculation of caustic.

Contacting Methods.—The design of *mixing columns* is normally based on the pressure-drop that is available for mixing. A total pressure-drop of 30 lb. per square inch is sufficient to give effective mixing, and many refiners find that mixing is effective at much lower pressure-drops. The particular type of mixer is not important, but intimate contacting must be attained. At the same time, many refiners report that too intimate a mixing gives difficulty in the settling and suggest only a pump and several sharp-angle turns for mixing. Among the types of mixers that are used are square-angle bends, orifice-plate columns, baffle-plate columns, perforated buckets, various mechanical mixers operated by motors, jet or nozzle mixers, and pumps. Irwin[37] describes a multiple-cone type of mixer and the

[37] *Oil Gas J.*, July 19, 1934, p. 10.

computation of the pressure-drop through the mixer. Mechanical mixers usually consist of a shaft with blades attached. Pumps give fair mixing, particularly centrifugal and rotary pumps, but additional mixers and baffle columns for prolonging the time are usually used. An ingenious use of a centrifugal pump for mixing is mentioned by Morrell and Bergman.[38] The impeller of the pump is cut down to about half diameter, and the impeller is reversed in the case.

The *orifice column*[38] is widely used for mixing. With an average orifice discharge coefficient of 0.65, the permanent loss is about 95 per cent of the pressure differential. Using these figures and when expressing velocity as barrels per hour, the following formula results:

$$\text{Bbl. per hr.} = 17.8D^2\sqrt{\Delta h} \tag{113}$$

D = diameter of orifice hole, in.

Δh = pressure-drop across one plate, expressed as head of liquid, ft.

The accuracy of this equation is influenced by the arrangement of the orifice hole or holes and by the ratio of the area of orifice holes to the area of the pipe, but great accuracy in the design of a mixing column is not justified. In general, the ratio of pipe area to the total orifice area may range from 3 to 10 and still be satisfactory. Inasmuch as the equation is to be used for only approximate results, Table 97 will prove to be a useful simplification. The figures within the block are the pressure-drops normally employed. The feet of liquid may be converted to pounds per square inch by the following relation:

$$\text{Lb. per sq. in.} = (\text{ft. of fluid}) \times (\text{sp. gr.}) \times 0.433$$

or

$$\text{Lb. per sq. in.} = \frac{\text{ft. of fluid}}{2.148 + 0.01623\ (\text{A.P.I.})} \tag{114}$$

The mixing column may be assembled by welding, by cutting slots at 1-ft. intervals and on opposite sides of the pipe. The plates are cut with a recess on one side (as thick as the pipe) so that one side of the plate fits against the inside of the pipe and the other side extends through the slot so that it can be welded. Another way to assemble the column is to use flanged spools with a plate between each spool. The plates may also be strung on rods, spot-welded, and slipped into the column from the end.

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[38] Three articles, *Chem. Met. Eng.*, **35**, 210, 291, 350 (1928).

If a longer time of contact is desirable, so-called *contact columns* or time columns may be used. These are attached after the mixing columns as shown in Fig. 177. Time columns may consist of large pipe with half-moon baffles or orifice plates having large holes. In arranging mixing equipment, no low points in which the chemical may collect should exist, because the liquid tends to surge in slugs into the settling equipment.

TABLE 97.—PRESSURE-DROP THROUGH ORIFICE MIXERS

Bbl. per hr.	Pressure-drop for each orifice plate, expressed as ft. of liquid for the following areas of orifice (total), sq. in.						
	0.4	0.6	0.8	1.0	3.0	6.0	10.0
10	1.2	0.54					
20	4.7	2.15	1.11	0.52			
40	18.8	8.6	4.45	2.08	0.35		
60	42.2	19.3	10.0	4.67	0.8		
100	.....	53.7	27.7	13.0	2.22	0.57	
150	.....	.....	62.5	29.2	5.0	1.29	0.45
200	.....	.....	.....	52.0	8.9	2.3	0.79
300	.....	.....	.....	.....	20.0	5.2	1.78
500	.....	.....	.....	.....	.....	14.2	4.95

If the chemical is injected by gravity feed or from a pressure feed-tank, the rate of feed can be controlled with a valve and no metering device is necessary. If blow-cases are used, the chemical must be measured as it is added. The most common method of metering is by orifice meters. Morrell and Bergman[38] present orifice meter charts. The treater often estimates the material handled by a blow-case by noting the time and the pressure during the admission of acid.

Example 82. Design of Orifice Mixer.—Acid is to be mixed with 8,000 bbl. per day of 53 A.P.I. pressure distillate. A pressure-drop of 25 lb. per sq. in. is permissible.

$$\text{Bbl. per hr.}\quad \frac{8,000}{24}\quad 334$$

Use about 7 sq. in. of orifice holes or openings.

Use a pressure-drop, feet of fluid (Table 97), of about 5.5 ft.

$$\text{Pressure-drop, lb. per sq. in. per plate} = \frac{5.5}{2.148 + 0.01623(53)} = 1.83$$

$$\text{Number of plates} = \frac{25}{1.83} = \text{about } 14$$

Use a pipe having about five times the orifice area, or 30 sq. in. Use standard or extra heavy 6-in. pipe with a transverse area of 28.9 sq. in.

Approximate layout of plates:		Sq. In.		Sq. In.
Six 1¼-in. holes	6 × 1.227 = about	7.37		
or twelve ⅞-in. holes	12 × 0.601 = about	....		7.22
1/16-in. clearance around one side of plate.............	=	0.42		0.42
Total opening, sq. in.	=	7.79	or	7.64

The plate will be 6.07 in. in diameter with a 1/16-in. recess around half of the circumference.

If the plates are spaced 1 ft. apart, the total length of the mixing column will be about 16 ft.

In rare instances the time of contact must be very short, and for such situations mechanical mixers like those employed in the centrifuge treating systems[39] may be employed. Refer to Fig. 180 (page 603).

Settlers or Separators.—The exact *settling time* that is required must be determined for each treating operation. In general, caustic and water mixtures settle more rapidly than acid sludge or "pepper." Ten or fifteen minutes often suffices for caustic or doctor settlers, but an hour may be required for settling acid sludge. The settlers are usually about 40 ft. high and range in diameter from 2 to 10 ft. In large-diameter tanks, a gentle circulation takes place and tends to spoil the separation. The sprays for water-wash tanks are usually of welded pipe in the form of a cross or a six-legged star with ⅛-in. holes drilled on the same side of each pipe in the star. These sprays, all pointed in the same direction, give a gentle rotating motion to the oil in the tank. They are placed several feet below the oil outlet. Horizontal settling tanks are more effective than vertical settlers of the same capacity. This is due to the lower vertical velocity in the horizontal settler. The velocity of the fluid in the settler should not exceed about 3 ft. per minute. A higher velocity will require a greater time for settling. Stokes's law (page 385) governs the rate of settling.

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[39] TRIVALS, H., *Ref. Nat. Gaso. Mfr.*, May, 1932, p. 312.

Example 83. Design of Settlers.—A tank for settling caustic from 12,000 bbl. of oil per day may be designed as follows:

Caustic or doctor settler:

Allow 30 min. of time, and use a vertical tank 40 ft. high.

$$\text{Volume of oil per hr.} = \frac{12{,}000}{24} \times \frac{42}{7.5} = 2{,}800 \text{ cu. ft.}$$

$$\text{One-half of this} = \frac{2{,}800}{2} = 1{,}400 \text{ cu. ft. to be handled in 30 min.}$$

$$\text{Cross-section area of settler} = \frac{1{,}400}{40} = 35 \text{ sq. ft.}$$

Diameter = about 6 ft. 10 in.

If 40-ft. tanks are not convenient, then two 20-ft. tanks connected in series can be used.

Acid sludge settler:

Allow 1 hr. and use a 40-ft. tank.
Cross-section area = 35 × 2 = 70.0 sq. ft.
Diameter = about 9 ft. 6 in.

Concentrated sulfuric acid, acid sludge, and caustic solutions do not attack steel rapidly, but dilute acid reacts violently so that water-wash tanks after acid-settling tanks must be lead lined. The caustic settlers and caustic water-wash tanks are also frequently lined with lead, although lead linings are not really necessary. Self-lubricated cocks, such as the Merco-Nordstrom or MacGregor, should be used on the chemical lines. Steel pipe is used for all connections except the drain lines from acid-water-wash tanks. These lines should be lead lined or constructed of alloy cast iron. The drains should have air or steam connections into them so that they can be "blown out" in case they become plugged with sludge or scale.

In acid treating, some refiners[40] have found that neutralization and coagulation with clay are more satisfactory than settling and neutralization with caustic. The use of a Hardinge clarifier is reported.[40] The sludge is collected on a bed of sand, and revolving paddles continually scrape the sticky sludge from the top of the filter. The thickness of the bed is finally so decreased that new sand must be added. Still other refiners[41] utilize vessels packed with rock or sand.

Filter Presses.—Solids are usually in a finely divided condition, and hence filter presses rather than gravity settlers are often necessary. The only major use of filters is in removing finely divided clay from treated cylinder stock in the clay-contact process. The Sweetland press, a picture of which is shown in Fig. 175, is widely used, and more recently the Oliver precoat continuous rotary filter has been adopted by some refiners. In addition the Kelly pressure filter[42] is used for removing carbon, lime, and other solids from cracking-still residuum. Pressure filters are also used to remove clay from pressure distillate.[39]

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[40] WILLSON, C. O., *Oil Gas J.*, Dec. 18, 1930, p. 38.

[41] VESPER, H. G., *Oil Gas J.*, Mar. 30, 1933, p. 44.

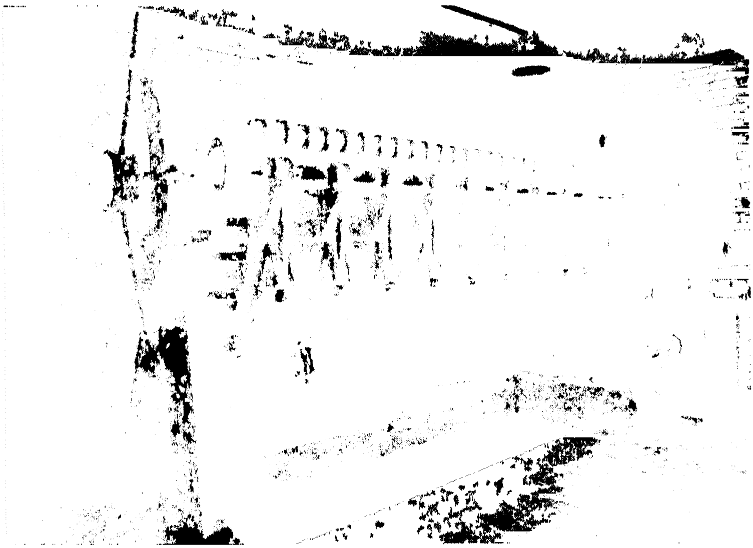

FIG. 175.—Sweetland filter press for removing fine clay. (*A. J. Smith Engineering Company.*)

The Sweetland press[42] consists of a cylindrical horizontal shell having a hinged bottom, half of which can be dropped down for removal of the filter clay. Circular filter leaves are arranged crosswise in the shell, each being suspended by a separate connection at the top to an oil-discharge manifold. The oil-clay slurry is pumped into the shell through a manifold along the bottom. The oil passes through the sides of the leaves by application of a pressure of 40 to 50 lb. per square inch until a suitable cake thickness is attained. The cake is then washed with naphtha, steamed until dry, and then removed by opening the bottom of the press, which allows the cake to drop into a conveyor or discharge chute. Sizes range from 10 to 1,000 sq. ft. of filter surface. Difficulties and methods of handling filter clay or cake are discussed by Trescott.[43]

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[42] BADGER and McCABE, "Elements of Chemical Engineering," McGraw-Hill Book Company, Inc., New York, 1936.

The *Oliver precoat filter* is a modification of the regular Oliver filter.[42] It consists of a horizontal cylindrical drum, the outside of which is made up of separate segments or compartments. The entire outside of the cylinder is covered with a filtering medium such as fine mesh wire or cloth. Each segment is connected to a discharge line, under vacuum, by a special valve on the end of the drum in such a way that suction is maintained while the drum rotates. A deposit (or precoat) of a special filtering medium or clay is built up on the drum by rotating the drum for about 30 min. in a vat containing a slurry of the precoat filtering medium. The vat is then filled with the oil-clay mixture; and as oil passes through the filter surface, a thin film of clay is deposited on the surface of the precoat. The thin layer of clay is continuously shaved from the surface by means of a knife edge until the precoat is consumed. The precoat lasts from several hours to as long as several days, depending upon conditions. The coating of clay may be washed with naphtha and dried with air or steam as the drum revolves.

PRACTICE OF TREATING

The foregoing discussion of the chemistry, fundamentals, and equipment of treating was so involved that the manner of conducting these processes could not be discussed. Many different arrangements of equipment have been successfully used as well as the particular arrangements or diagrams that are shown in the following pages.

Natural Gasoline.—About three-fourths of all the natural gasoline that is manufactured in the United States is treated by the hypochlorite process. The treating equipment is simple because practically no sludge is produced and the chemical is easily handled. If bleaching powder or a very strong variety referred to as H.T.H. is used, the plant consists merely of a chemical solution tank, a mixer, and a settler.

Figure 176 shows a hypochlorite treater. The gasoline is normally sprayed through the treater, and the hypochlorite chamber is not used. When the chemical is spent, the valves that are shown in the diagram can be opened and the solution is pumped through the chamber to dissolve additional chemical. The chamber can be opened and refilled with chemical without molesting the treating operation.

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[43] *Ref. Nat. Gaso. Mfr.*, February, 1934, p. 54.

The chemical is added once a day through the top of the settling tank, and the solution is recirculated, as required, through the mixing column. Simple mixing devices that utilize the gasoline supply through an aspirator cone, for sucking the solution into the system, have been successfully used.[44]

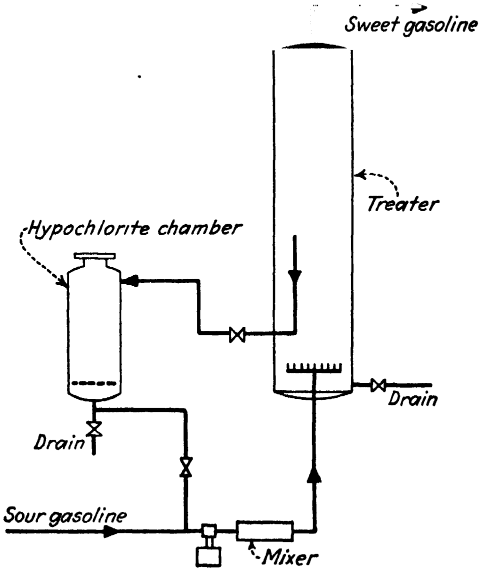

FIG. 176.—Hypochlorite sweetener for using bleaching powder.

If hydrogen sulfide is present in more than traces, the gasoline should be first washed with water or caustic. From 1 to 4 lb. of H.T.H. or 4 to 25 lb. of bleaching powder per thousand gallons of gasoline is normally required.

Straight-run Gasoline.—A caustic wash or a sweetening treatment is all that is normally required for straight-run gasoline, and some of these gasolines require no treatment at all. In simple caustic treatment, the system shown in Fig. 174 may be used. The caustic settling tank can be charged once daily (or less often) with fresh caustic and circulated until it is spent. If the gasoline is unstable to light, a filtration through coarse fuller's earth is often helpful. Doctor sweetening may be conducted in equipment similar to the last part of the flow diagram shown in Fig. 177. The sludge filter shown in this diagram is not widely used. Some treaters believe that doctor sweetening is more successful if the sulfur is added after the doctor solution rather than as shown in Fig. 177.

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[44] Treating Natural Gasoline . . . , *Ref. Nat. Gaso. Mfr.*, July, 1933, p. 278.

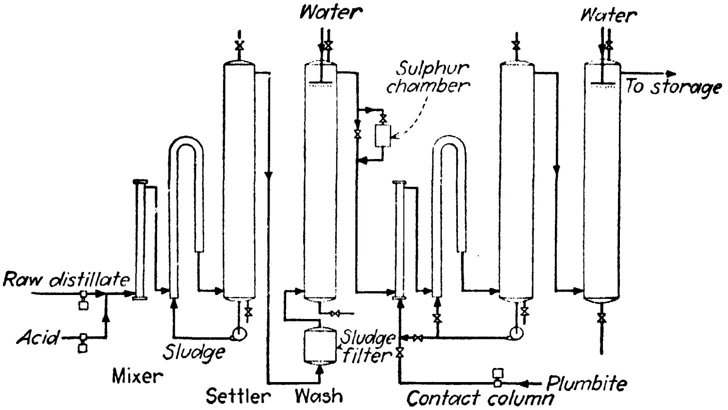

FIG. 177.—Continuous pressure distillate treater.

Occasionally the sulfur content is so high that acid treatment must also be used, and the general manner of handling such a gasoline may be found under the next topic.

Doctor sweetening may also be conducted in a batch system by using an agitator. The advantageous effect of air agitation upon the sweetening is recognized, but the vapor losses may be great.

The *copper sweetening* (page 600) process holds some advantages over the caustic washing and doctor processes because of its simplicity. The dry process[45] is suitable in most instances for handling natural or straight-run gasoline, but the wet process[31] is shown here because it can be applied to all stocks including even cracked distillates. A flow diagram of the process is shown in Fig. 178. Free sulfur and hydrogen sulfide are removed in the caustic wash; mercaptans are converted to disulfides by copper chloride; and any carry-over of sulfide is accumulated and recirculated as the final operation.

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[45] ANON., Perco Solid Copper Sweetening Process, *Ref. Nat. Gaso. Mfr.*, April, 1940, p. 73.

The *Solutizer process* (page 601) has the advantage of removing sulfur and hence may result in a product having a higher octane number, an increased susceptibility to the effect of tetraethyl lead, and more color stability. A flow diagram is shown[24] in Fig. 179. The steps in the process are caustic washing, solutizer washing to dissolve mercaptans, and stripping of the solutizer solution by means of steam. Contacting is effected by means of a countercurrent tower packed with carbon Raschig rings, and the process is completely continuous. It may be applied for the sweetening of any type of distillate including cracked, reformed, or poly distillates.

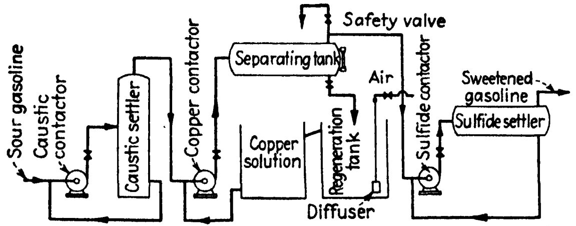

FIG. 178.—Flow diagram of copper (solution) process. (*Perco Corporation.*)

Pressure-still Distillate.—Such distillates contain gum which may be removed by acid treatment or by vapor-phase clay treating, or the formation of gum may be delayed by the use of inhibitors. Distillate also contains sulfur which in part must be removed by the sweetening processes just discussed, but it may also contain sulfur compounds that can be removed only by cold sulfuric acid treatment or catalytic processes.

The standard method of pressure-distillate treatment for many years was acid treatment, distillation of this material with steam, and doctor sweetening. This general procedure is utilized today to some extent for distillates that are high in sulfur. Acid treatment is usually conducted at prevailing temperatures in a continuous treater and neutralizer; but if the gasoline does not turn sour upon distillation, the treating may be simplified to an acid treatment and plumbite treatment in one operation

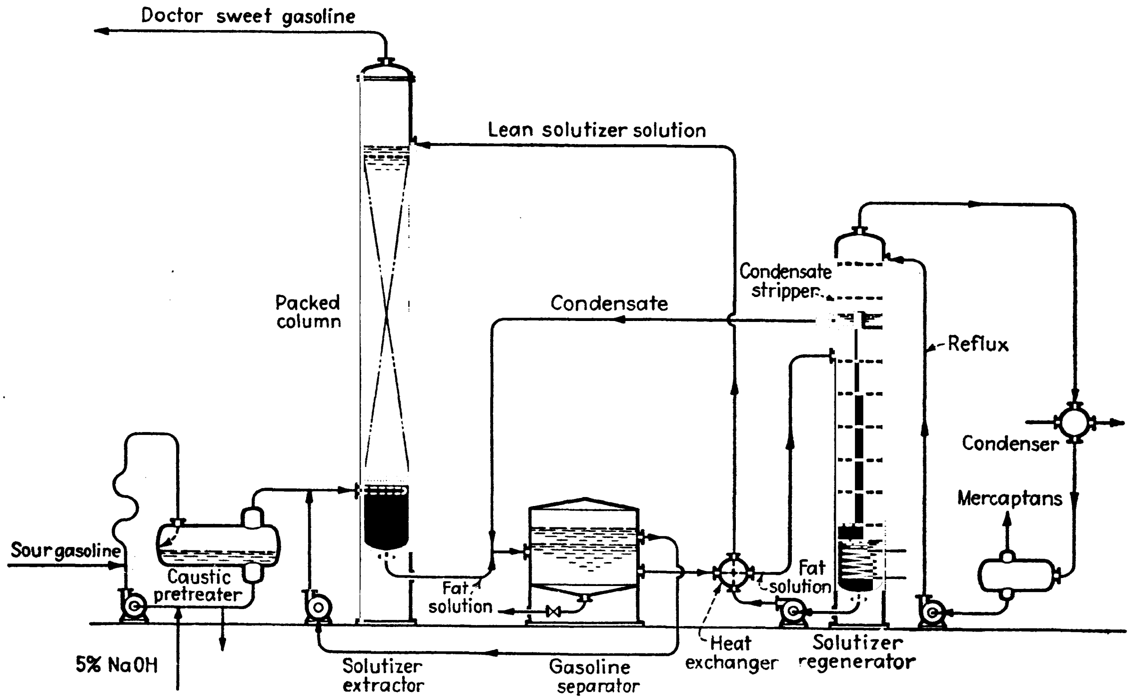

Fig. 179.—Flow diagram of Solutizer process. (*Shell Development Company.*)

(Fig. 177). Some refiners find that a double doctor treatment, one before and one after distillation, is necessary.

Other modifications of the continuous-settler type of system are sometimes useful. The arrangement of equipment for two of these are

A. Sludge-circulation treatment

1. Baffle column for pressure distillate and acid sludge.
2. Sludge settler. Sludge to waste.
3. Mixing columns for fresh acid.
4. Acid settler, sludge to 1.
5. Sludge filter.
6. Water wash.
7. Caustic mixers.
8. Caustic settler.
9. Water wash.

B. Split plumbite

1. Plumbite or caustic mixers.
2. Settler.
3. Water wash.
4. Acid mixers.
5. Settler.
6. Water wash.
7. Plumbite mixer.
8. Settler.
9. Water wash.

For high-sulfur oils, method *B* usually suffices, but occasionally the sulfur is not completely removed. Sometimes this may be remedied by applying the acid in several doses of about 2 or 3 lb. per barrel each and using a presludge treat before applying any acid. Some high-sulfur distillates require 20 lb. of acid per barrel.

Quick-contact and -settling Processes for Cracked Distillates.—These methods are attracting more and more attention. Whether they are used for distillates or lubricating oils, the advantages claimed are the smaller amount of acid that is required, the control that the processes afford, the advantages of continuous operation, and the smaller sludge losses.

A flow diagram of the Stratford contactor centrifuge process is shown in Fig. 180. The high-sulfur pressure distillate[8] is pumped from the caustic-wash tanks to the contactor in which it is mixed for 1 or 2 sec. by means of a rotating shaft with blades and fixed baffles. The oil is immediately transferred to the centrifuges, and the entire time of treatment including contacting, transfer, and separation of the sludge may be less than 4 sec.

The acid stage oil is then delivered to caustic treaters or contacted[39] with 200–300 mesh clay for a few minutes and filtered in Sweetland presses. The short time aids in avoiding polymerization of the valuable olefin hydrocarbons and thus allows the use of acid for desulfurizing high-sulfur cracked distillates without destroying the antiknock properties of the gasoline. At one time the development of quick-contact processes was at a standstill

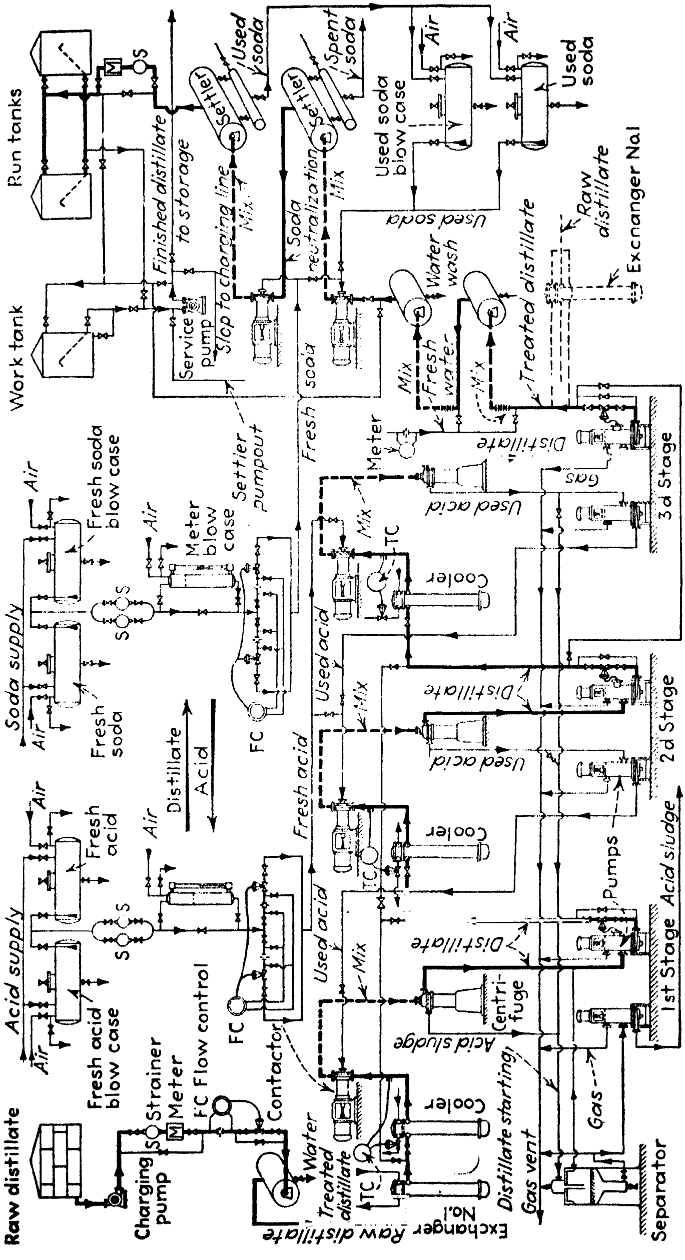

FIG. 180.—Stratford centrifuge treating system. (*Stratford Engineering Corporation.*)

because the gum was not thoroughly removed, but this difficulty has apparently been solved.

The process is well suited for desulfurization, and hence the latest developments of the process have been for *cold*-acid treatment.[46] The flow is similar to that shown in Fig. 180 except that refrigeration, heat exchangers, and chillers are required. A recent plant[46] utilized gravity settlers rather than centrifuges.

Clay Processes for Cracked Distillates.—The *Gray vapor-phase*, the *Osterstrom liquid-phase*, and the *Stratford continuous*[47] processes are the outstanding examples of clay processes for treating cracked distillates. They cannot be applied to high-sulfur distillates because they remove little, if any, sulfur, but they are effective and cheap for many cracked distillates. The principles underlying the three processes are the same. Most of the diolefin and other gum-forming hydrocarbons are removed, but other hydrocarbons are only slightly attacked. Most low-sulfur distillates can be successfully treated, but the distillates from some California oils have given difficulty with color stability. The vapor-phase process is not usually applied to distillates from vapor-phase cracking processes because the action is too vigorous and results in the removal of valuable hydrocarbons such as the olefins. The Osterstrom process was developed to meet this need. The clay processes are to some extent being supplanted by the use of inhibitors.

In the *Gray process* the vapor from the cracking tower is taken through towers that are packed with clay. Polymerization occurs, and a polymer liquid, containing a large percentage of gasoline, collects in the bottom of the tower (Fig. 181). The polymers may be injected into the bubble-tower or evaporator of the cracking system so that the gasoline is recovered and the pure polymer either finds its way into the tar or is recracked. The vapor passes on to the condensers and is a finished product except for sweetening.

Goode[48] has made an extensive study of color and gum content as related to vapor-velocity and the depth of the bed of clay. A

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[46] Stratcold Treating Process . . . , *Ref. Nat. Gaso. Mfr.*, July, 1939, p. 267.

[47] Gray, by independent refiners; Stratford, by Imperial Oil Co., Ltd.; Osterstrom, by The Pure Oil Co. respectively.

[48] *Ref. Nat. Gaso. Mfr.*, December, 1931, p. 79.

30–60 mesh clay is commonly used, but 60–90 clay is used by some refiners.

The throughput per ton of clay is often 3,000 to 5,000 bbl., and one plant is reported to have processed 20,000 bbl. for each ton of clay. The yield per ton of clay is greatly increased by eliminating entrainment in the gasoline vapor line. One refiner uses a mist extractor for this purpose. The clay chambers range in size from 6 to 16 ft. in diameter and in height from 25 to 40 ft.

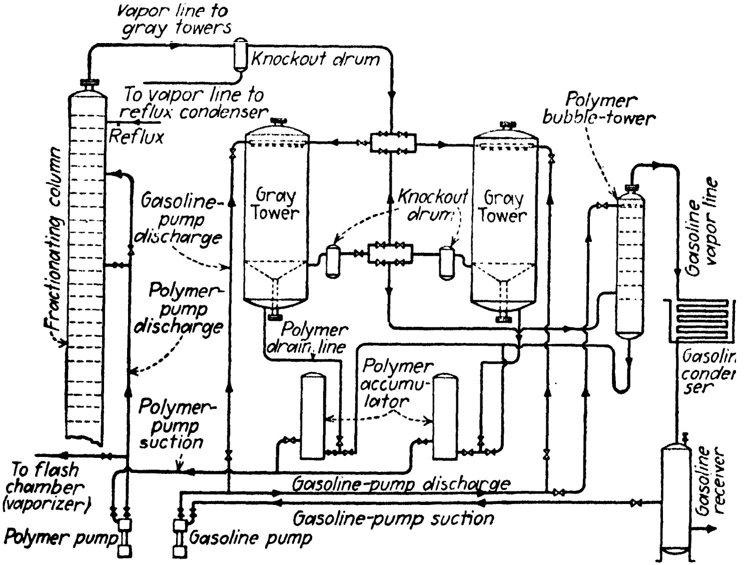

FIG. 181.—Diagram showing series-parallel arrangement of Gray towers. (*Gray Processes Corporation.*)

In the *Stratford process* the vapor ascends the treating tower countercurrently to a stream of descending clay slurry. The spent clay slurry is continuously settled in cone bottom tanks and dried continuously with hot flue gas and a vacuum. About 1,000 bbl. of distillate can be treated per ton of clay, but the gallonage varies because the amount of slurry can be regulated to obtain different degrees of treating. The flexibility of the process is one of its main advantages.

In the *Osterstrom process* the cracked distillate is heated, as a liquid, in a conventional pipestill to about 500 to 600°F. It flows under pressure (no vaporization) through a bed of adsorbent, such as 30–90 mesh fuller's earth, and back into a short coil in the pipestill. It issues from the still at a temperature high enough to cause vaporization when the pressure is released. The vapor is fractionated to end-point in a tower, and the polymer is separated as a bottoms product. The high temperature facilitates the action of the clay so that as much as 70,000 bbl. of gasoline have been treated per ton of clay. However, vapor-phase gasoline is seldom treated to the high colors that are required in other gasolines.

Clay is sometimes used as a neutralizer for acid-treated pressure distillate[39] as in the clay-contact process for lubricants. The clay is removed by pressure leaf-type filters. About 1 to 5 lb. of 200 mesh clay per barrel is required to neutralize the acid.

Catalytic Processes.—Most sulfur compounds except possibly cyclic ones are decomposed by heating to 700 to 750°F. in the presence of bauxite.[49] The reduction of sulfur to such low values as 0.002 to 0.01 per cent results in high octane numbers and makes tetraethyl lead particularly effective in increasing the octane number. The gum content and other properties of the gasoline are not greatly affected. Thus far, the process has been applied to only natural and straight-run naphthas.

In the Houdry treating process,[50] a diagram of which is shown in Fig. 182, gasoline vapor at about 645°F. and at a pressure of 50 lb. per square inch is passed upward through a hydrated silicate of alumina catalyst which also contains oxides of nickel, cobalt, or other metals. The catalyst is poisoned during 3 to 10 hr. of use and hence must be regenerated by passing heated air through it to oxidize the carbon and sulfur deposits. About 3 hr. are required for regeneration. During regeneration the catalyst temperature is kept down to 1000°F. by means of a jacket through which is passed a circulating stream of molten sodium nitrates and nitrites. The process produces a color-stable, low-sulfur, low-gum gasoline of high octane number. The product is well suited for aviation gasoline because of its low "acid-heat" value.

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[49] SCHULZE and ALDEN, Catalytic Desulfurization . . . , *Oil Gas J.*, Nov. 17, 1939, p. 199.

[50] NORMAN, H. S., *Oil Gas J.*, Mar. 28, 1940, p. 106.

Kerosene.—The quantity of kerosene that is manufactured in most refineries is relatively small, and hence batch agitators are still used by small refiners. The batch agitator is nothing more than a large mixing and settling tank. Cylindrical shells with conical bottoms having a pitch of 4 to 6 in. per foot are used. Connections are provided for injecting chemicals, for introducing wash water through sprays, and for an air-line with which to mix or "roll" the chemical and the oil. Although large vapor losses occur with air agitation of distillates, the mechanical methods of mixing, using a circulating pump or paddles, are not entirely satisfactory because of the time required for complete mixing.

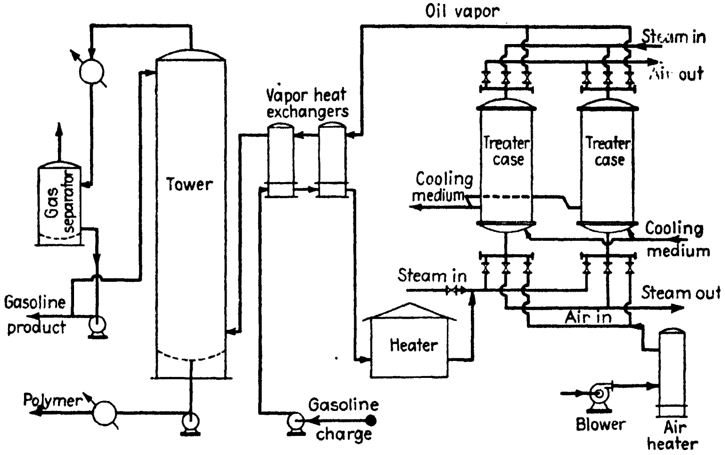

FIG. 182.—Houdry catalytic treater for gasoline. (*E. B. Badger and Sons, Company.*)

The batch treatment of kerosene varies greatly depending upon the characteristics of the raw stock. For normal kerosenes the acid requirement is 3 to 6 lb. per barrel, but kerosenes that are rich in aromatics may require 30 lb. per barrel, part of which may be fuming acid. One Pennsylvania refiner[51] reports the successful use of hypochlorite in treating kerosene, but such a treatment is probably unfit for most kerosene stocks. A typical batch acid treatment for kerosene is as follows:

1. Agitate with acid 30 min. Often the acid is split into a small dose of "water-acid," and after this is drained, the main acid is admitted.

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[51] KIRKWOOD, G. M., *Petroleum Eng.*, February, 1932, p. 108.

2. Settle ½ to 1½ hr.
3. Spray with water for two 15-min. periods, and drain.
4. Spray with soda and wash with water, 15 to 30 min. Drain.
5. Wash with water 15 min. at about 100°F.
6. Settle 45 min. to 2 hr.

In the manufacture of prime kerosene from naphthene-base crude oils the following procedure may need to be used:

1. Agitate with water-acid (1 lb.), 15 min.
2. Settle. Drain.
3. Three treats of 8 lb. each of fuming H_2SO_4; settle and drain after each.
4. 3 lb. treat with 66°Bé. acid. Drain.
5. Three washes with water, agitating during wash, 15 min. each.
6. Neutralize with 6 lb. of 12°Bé. caustic.
7. Settle and drain.
8. Two washes with water, 15 min. each.
9. If color is not satisfactory, filter through fuller's earth or agitate with about 0.4 lb. of earth.

Methods of improving the color are (1) redistillation with steam as with pressure distillate and (2) filtration through fuller's earth. Continuous methods of acid treating kerosene are in operation in many Mid-Continent refineries. The treating of kerosene from mixed-base and paraffin-base oils is usually not a difficult operation. For the removal of aromatics, as from naphthenic crude oils, the Edeleanu solvent extraction process is widely used.

Lubricating Oils.—There is such a wide variety of heavy oil stocks and the treatments that are used differ so greatly that only a few general operations can be discussed. Oils are treated with acid, filtered through clay in percolation filters, contacted with clay at a high temperature, or treated by solvent extraction methods. Pennsylvania stocks can usually be finished by percolation or clay contacting without acid treatment, but other oils usually require acid treatment. Solvent extraction is discussed in Chap. XXVII.

The acid treatment of lubricating oil stocks is usually conducted in batch agitators. However, note the discussion of continuous lubricating oil treaters (page 609). Inasmuch as the characteristics of oils vary greatly and the details of treating various oils are so different, the operations can be best illustrated by the operations of several refiners:

	Distilled cyl. stock	Residual cyl. stock	225 neutral	Pale oils	Average oils
Refiner	I	I	I	II	III
Pounds water acid, 66°Bé., agitate ½ hr	4	32	1	4	2–12
Hours of settle and draw	6	4	2	4	2–31
Pounds acting acid, 66°Bé., agitate ½–1 hr	8	......	4	10–18*	20–60
Hours of settle and draw	5	......	9	12–20	2–8
Water-wash	......	......	(150 gal. per 1,000 bbl.)		Yes
Neutralized by	Clay contact	Clay contact	Clay contact	Caustic	Caustic

* 98 per cent acid.

Neutralization with soda ash or caustic is accomplished by agitating gently with 3 to 15°Bé. caustic until neutral, spraying with hot water or steaming, and settling for 4 to 15 hr. Several washings and settlings are usually necessary. The oil may then be brightened by heating to 120 to 200°F. by steam coils in an open pan; heating and blowing with air; or by agitating with dry Sil-O-Cel, etc., and filtering.

Neutralization with caustic or soda is a troublesome operation because of the frequent formation of emulsions. Often these emulsions are of such stability that only a repeated acid treatment or an application of strong caustic will cause a separation. For this reason, neutralization is being more and more frequently accomplished by the use of clay, as in the contact process, or with ammonia.

The use of centrifuges is also being promoted for the treating of lubricating oils.[14,15] In general the oil is heated and mixed with acid for about 10 min. by a mechanical mixer and/or reaction tank. It is then "soused" with water to prepare the sludge and discharged through the centrifuges. The sludge accumulates in a hopper and is continuously pumped to fuel oil mixing tanks or to an acid recovery system. The acid is sometimes added in two portions, one portion as outlined above and a second dose at the centrifuge itself. The latter dose of acid aids in producing a fluid sludge. In one plant the sludge was removed from the bowl of the centrifuge by means of hot fuel oil. The properties of lubricating oil sludge vary so widely[16] that each continuous lubricating oil treater is a new problem. Cylinder stock has been treated in some of these plants without dilution.

The success of continuous treatment of lubricating oils always depends upon a method for removing the sludge. Cone settlers have been used to some extent.[16] The sludge accumulates continuously in the bottom of the cone, and the oil overflows continuously from the entire periphery of the top of the cone. Thus, the oil is skimmed from the top of the settler without causing the currents in the fluid that a connection in the side of the cone would produce.

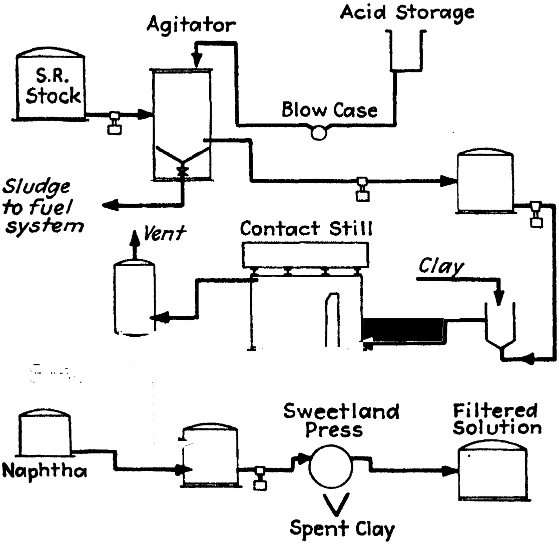

Fig. 183.—Diagram of clay contact treating process.

Contact Filtration.—The most common method of neutralizing with clay is the contact process. In addition the process effectively decolorizes the oil. Contacting is usually practiced on oil that is in the "acid-stage" or, in other words, oil that has been treated with acid but not neutralized. The clay is rendered more effective if the oil is acid.

The process is practiced at 220 to 650°F., but most refiners contact diluted cylinder stocks at 475°F. and neutral oils at 220 to 320°F. Occasionally lower temperatures are used, but such an operation should be classed as neutralization. The acid-stage oil is mixed with 200 or 200–300 mesh clay, and the mixture is heated in a pipestill to the aforementioned temperatures. The hot oil is then allowed to settle for a short time, and the "fines" (clay dust) are filtered from the oil in Sweetland or similar presses. Sometimes a short percolation filter is used to aid in the removal of the fine clay. The clay is not usually recovered, although experiments are constantly being made in an effort to reactivate the clay by solvent methods. Figure 183 illustrates the general equipment in a contact plant.

The more viscous oils, such as cylinder stock, are usually acid treated and contacted in solution. The solution contains between 50 and 75 per cent of a high-initial-boiling-point naphtha. The naphtha usually has a boiling-range of 160 to 400°F. Dilution is necessary for the subsequent operation of centrifuge dewaxing, and it also simplifies the handling of the stock during the acid treating and contacting operations. In addition, Trescott[16] reports that the amount of dilution vitally affects the losses during acid treatment. In treating a Mid-Continent residuum (U.S. 130 at 210) with 30 lb. of acid per barrel, the losses were as follows:

Per Cent Naphtha in Solution	Per Cent Treating Loss
None	31
25	23
50	14
75	14

The decrease in loss is doubtless due to the fact that less oil is contained in the sludge if the stock is diluted. The neutral oils are usually contacted without diluting them, but they must be heated to a sufficiently high temperature to cause them to be fluid.

Although the contact process yields excellent products, it may be more expensive[52] than percolation, particularly if an efficient clay-burning system is available. However, the cost of installing a complete percolation system is great, and contacting is probably the cheaper method for a new installation. In the contact process, the amount of clay that is required ranges from 5 to 25 per cent of the weight of the oil. This amounts to 15 to 80 lb. per barrel.

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[52] Davis, L. L., *Ref. Nat. Gaso. Mfr.*, March, 1928, p. 90.

Percolation.—Percolation was the original method of decolorizing lubricating oils, and until recently no other method of using clay was widely employed. Gurwitsch[53] says,

> The advantage of filtration consists in the better utilization and smaller expenditure of the adsorbent to produce a given degree of decolorization . . . the oil comes successively into contact with a great number of very thin layers of the adsorbent, the filtration is equivalent to an extremely fractionated mixing, and so its effect on the reversibly adsorbed substances must be greater than that of mixing, even when carried out in several operations with equal quantities of adsorbent.

Regarding the percolation method, Funsten[54] says,

> Thus, percolation permits the manufacture of a wide variety of oils at one time. White oils or petrolatums of varying degrees of refinement can be processed with it equally as well as cylinder oils. . . . Specialties can be made at little, if any, extra cost by selection of proper cuts from the filter stream. Waxes, gasoline, kerosene and furnace oil can be clarified with revivified percolation clay at extremely low cost, since yields are very large in this type of work.

In general, for gravity flow, the longer the packed column the greater the bleaching action, the coarser the earth the less the bleaching, and the higher the temperature the less the bleaching (other conditions being comparable). Bauxites and fuller's earth are used almost entirely. The efficiency as a function of particle size is somewhat as follows:

Mesh	Per Cent Efficiency
60–90	100
30–60	87
16–30	72

However, a 30–60 mesh material is most commonly used because it can be more easily handled. Although the temperature should not be so high that the oil drains through the clay with only a short time of contact, nevertheless viscous lubricating oil stocks must be heated or the rate of percolation will be hopelessly slow. Operating conditions[54] for a 1,000-cu. ft. filter are given in Table 98.

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[53] "Scientific Principles of Petroleum Technology," 2d ed., D. Van Nostrand Company, Inc., New York, 1924.

[54] *Ref. Nat. Gaso. Mfr.*, June, 1934, p. 201.

TABLE 98.—OPERATION OF FILTERS

Stock	Saybolt viscosity	Temp. of filtration, deg. F.	Rate of filtration, bbl. per hr. for a 1,000-cu. ft. filter	Pressure filtration,* lb. per sq. in.
Light spindles...............	Up to 200 at 100°	80–100	5–25	0–25
Heavy spindles..............	200–500 at 100°	100–140	5–15	0–25
Overhead or residual cylinder stock....................	100–160 at 210°	160–200	2–10	15–50
Naphtha solutions of cylinder stock....................	....	100–130	30–50	5–15
Petrolatums................	100–160 M.P.†	25° above M.P.†	5–20	0–15
Waxes......................	100–160 M.P.†	25° above M.P.†	5–20	0–15

* Pressures in the higher range are required where 60–90 mesh earths are used.
† Melting-point.

The stock may be acid treated before percolation, but it is usually neutralized before it enters the filters. The percolators should be insulated to promote a constant rate of flow. The clay is washed with 56 A.P.I., or lighter, naphtha to remove the oil from the clay. The filter is then steamed, and the clay can be removed by allowing it to flow from the bottom of the percolator. An important consideration is the recovery of oil from spent filters by washing with naphtha and steam. The viscosity of the oil, amount of naphtha for washing, rate of draining, recycling of naphtha, and other factors related to the recovery of oil have been thoroughly discussed by Ridgway, Henderson, and Ross.[55]

The throughput of percolators cannot be definitely stated because of the differences in stocks, differences in clays, and the degree of decolorization that is practiced. In a general way, 8 to 21 bbl. of finished-color motor oils can be filtered per ton of clay. For lighter finished colors, the capacity ranges from 4 to 8 bbl. per ton, and for darker finished oils, such as dark-red oils and cylinder stocks, as much as 25 bbl. per ton may be filtered. Funsten[54] reports that rates of 40 to 50 bbl. per hour can now be obtained. As high as 32 bbl. per ton of cylinder stock in the form of 50-50-600° stock solution has been filtered through new clay.

The burning of clay is conducted at 1100 to 1200°F. The average efficiency of mixed clay that has been burned from one

[55] *Oil Gas J.*, Nov. 18, 1938, p. 154; or Annual Meeting, A.P.I., Chicago, 1938.

to six times is about 60 per cent. In general, the clay may be burned six to eight times in Moore, Brockway, Rotary, and Kuebler burners and as many as forty times in the Nichols-Herreshoff burner. However, it is not usually economical to burn the clay more than ten or fifteen times in the Herreshoff burner.

In general, the refiner uses new clay for light-colored low-viscosity lubricating oils, and the heavy oils with a darker allowable color are decolorized by this same clay after it becomes unfit for decolorizing light oils. Thus the various used clays progress through the plant in a countercurrent manner so that the new earth meets light-colored stocks and the nearly spent earth meets dark-colored stocks.

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CHAPTER XXVII

SOLVENT TREATING OR EXTRACTION PROCESSES

Although the use of solvents for treating and dewaxing has been proposed for many years, not until about 1933 did commercial operations appear. Prior to that time the recovery of the solvent had been so ineffective that commercial developments were not feasible. The general purpose of the solvent processes is to separate a general group of offensive materials or hydrocarbons from the oil. As examples, propane deasphaltizing removes dark-colored resinous materials; liquid sulfur dioxide extracts unsaturated and aromatic hydrocarbons from kerosene; the Solutizer process removes mercaptans from gasoline; and furfural (and other agents) treating produces lubricating oils of high Viscosity Index.

Just as vacuum distillation permits the processing of black crude oils for lubricants, so the solvent processes tend to erase the old crude oil marketing system by which only a few crude oils were considered satisfactory for lubricant manufacture. By solvent methods, the original properties of the oil can be changed so that a uniform grade of oil can be manufactured from a wide variety of crude oils. Of the many[1] processes that have been proposed it now appears that the furfural,[2] Duo-Sol,[3] Phenol,[4] Edeleanu,[5] and Propane[6] processes have established their usefulness. The total capacity of lubricating oils now (1941) being processed by solvent extraction in the United States well exceeds 100,000 bbl. per day.

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[1] *Chlorex*—Bahlke, Brown, and Diwoky, *Oil Gas J.*, Oct. 26, 1933, p. 60; *nitrobenzene*—Meyers, W. A., *Oil Gas J.*, Mar. 19, 1936, p. 81; *crotonaldehyde* and *acrolein*—Poole and Wadsworth, *Ref. Nat. Gaso. Mfr.*, November, 1933, p. 412; *aniline*—Chappell and Ziser, U.S. Pat. 1,741,555, Dec. 31, 1929; *others*—Kalichevsky, V. A., "Modern Lubricating Oils," Reinhold Publishing Corporation, New York, 1938.

[2] Bryant, Manley, and McCarty, *Oil Gas J.*, May 16, 1935, p. 50.

[3] Tuttle, M. H., *Ref. Nat. Gaso. Mfr.*, June, 1935, p. 289.

[4] Stines, D. E., *Oil Gas J.*, Mar. 19, 1936, p. 75.

[5] Cottrell, O. P., *Oil Gas J.*, Nov. 30, 1933, p. 64.

[6] McCleur, Dickinson, and Forrest, *Oil Gas J.*, Oct. 27, 1938, p. 174; and Nov. 18, 1938, p. 209; also Bahlke, Thiele, Adams, and Ginsberg, *Oil Gas J.*, July 22, 1937, p. 44.

General Processing.—The physical properties of the solvent govern to a large extent the general type of processing that must be employed. Thus, low temperatures and high pressures are advisable in handling such solvents as liquid propane and liquid sulfur dioxide; the partial solubility and the formation of a constant-boiling mixture in the system furfural-water require an intricate distillation system; and the high boiling-points of nitrobenzene, furfural, and cresylic acid necessitate the use of a vacuum in the distillation of these materials from oil. Properties of the principal solvents are given in Table 99.

TABLE 99.—PROPERTIES OF EXTRACTION SOLVENTS

	Boiling-point, deg. F.	Melting-point, deg. F.	Specific gravity	Specific heat, B.t.u. per lb.	Heat of vaporization, B.t.u. per lb.	Solubility in water, per cent at	
						77°F.	100°F.
Furfural (furfuraldehyde)…	323	− 34	1.162	0.416	193.5	8.5 (4.0 water in fur.)	9.0
Cresylic acid (Duo-Sol process)…	365–400	....	1.045	0.53	180	2.5	3.1
Phenol…	361	106	1.072	0.56	206	9 (∞ at 151°F.)	
Sulfur dioxide…	14	−105	1.45	0.32	167	(19 at 32°F.)	5
Chlorex (ββ′ dichloroethyl ether)…	352	− 61	1.222	0.37	115	1.1 (1.7 at 194°F.)	
Nitrobenzene…	411.5	42.5	1.207	0.34	142	0.2	0.25
Propane…	− 44	....	0.51	0.6 0.47 vap.	183	slight	
Benzene…	175	42	0.805	0.41	170	0.07	

Only a minor part of the total equipment in a solvent treating plant is devoted to the extraction operation. Elaborate equipment is required to distill the solvent (or oil) from the extract and raffinate solutions, to separate the last traces of solvent from the finished oils, and finally to recover the solvent from many sources and purify it. Thus, the design of solvent treating equipment resolves itself to a large extent into the design of equipment for the common operations of fractionation, absorption, stripping, etc., by methods that have been discussed in other chapters. Several general processing steps are used:

1. *Dry* or *deaerate* the charge-stock. Water hinders the action of phenol, and air is troublesome with gaseous solvents such as sulfur dioxide.
2. *Extraction with solvent.* The countercurrent method of contacting is used universally except for such special cases as the single contact used in propane deasphaltizing. The theory of liquid-to-liquid extraction was discussed briefly on pages 275, 280, Chap. XV.
3. *Separation of bulk of solvent* from oil. This is accomplished by heating and fractionating or evaporating. This is usually a simple operation because the oil and solvent have greatly different boiling-points, but the separation of gasoline and sulfur dioxide is an exception. A vacuum is used for the highest boiling solvents, but a simple atmospheric flash suffices for propane.
4. *Purification of oil.* The oil is freed from last traces of the solvent by steam stripping or, if water is troublesome, by vacuum flashing.
5. *Purification of solvent.* This may involve the removal of water as in the case of furfural, the separation of solvents from one another in case several solvents are used, or the separation of tars, etc., as in the Duo-Sol process.

A discussion of solvent processes is not complete or of much value without illustrations of the properties of the oils that are produced. Nevertheless, space does not permit such a discussion in this book, and hence the reader must resort to the current literature and the references given here.

Edeleanu Process.—This pioneer (1907) solvent process is the only one that has been applied widely to light distillates such as heavy naphtha, kerosene, and gas oil.[7] At the boiling-point of sulfur dioxide (14°F.), aromatic and unsaturated hydrocarbons are completely miscible with liquid sulfur dioxide but the paraffin and naphthene hydrocarbons are not. The process is used as a means of treating light distillates, but it cannot be utilized for high-boiling oils because their solubility in sulfur dioxide is too low. Lubricating oils can be treated, however, by using a mixed solvent of benzene and sulfur dioxide. Sulfur dioxide also extracts cyclic sulfur compounds and nitrogen compounds, a property that makes the process useful in handling certain high-sulfur kerosenes.

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[7] Dunstan *et al.*, "Science of Petroleum," Vol. III, Oxford University Press, New York, 1938.

The process has been applied to kerosene to improve the smoke point and for desulfurization.[7] It is applied to selected naphthas for the recovery of high-octane-number blending stocks and for the recovery of lacquer diluents (aromatic hydrocarbons).[8] Diesel fuels of high Diesel Index and ignition quality can be made from selected gas oils.

In treating kerosene the stock is first deaerated by exposure to a vacuum. The kerosene and liquid sulfur dioxide are then cooled by exchangers and coolers to 15 to 20°F. and contacted by countercurrent flow through a tower packed with rings. The cold raffinate and the cold extract are each passed through their respective exchanger and multiple-effect evaporator systems for the recovery of gaseous sulfur dioxide. The first stage of the evaporators operates at about 150 lb. per square inch and at 150 to 170°F., but the last stage is maintained at about 25 mm. pressure. The gaseous sulfur dioxide is compressed and condensed to a liquid.

The amount of solvent used depends upon the stock being handled, but in general it is about equal to the charge-stock. This results in an extract containing 10 to 20 per cent oil and a raffinate containing 15 to 20 per cent sulfur dioxide. Equilibrium curves for several stocks are given in "Science of Petroleum."[7]

The sulfur dioxide-benzene process[5] is the only mixed-solvent process that will be mentioned. It is widely used and derives much of its value from the ease with which the solvent can be recovered and purified. The processing is generally similar to that described for the liquid sulfur dioxide process. Sulfur dioxide-benzene may also be employed for dewaxing.[9]

Furfural Process.—The use of furfural for lubricating oil manufacture has recently been gaining in comparison with other solvents. Furfural is relatively cheap; it possesses a reasonable extraction efficiency; and adequate raw stocks are available for its manufacture.

The yield of high-viscosity-index raffinate varies with the stocks being treated but is about 70 per cent for intermediate-base stocks and 95 per cent for paraffin-base stocks. Yields from naphthene-base stocks are lower (65 per cent), and the Viscosity Index is necessarily low.[2,7] The general equilibrium relation between furfural and oil is indicated in Fig. 92 (page 279). Temperatures of 150 to 250°F. are employed, but most plants are operating at about 200°F. The amount of solvent employed also

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[8] SAEGEBARTH, BROGGINI, and STEFFEN, *Ref. Nat. Gaso. Mfr.*, June, 1937, p. 256.

[9] ANON., *Oil Gas J.*, Dec. 29, 1938, p. 131.

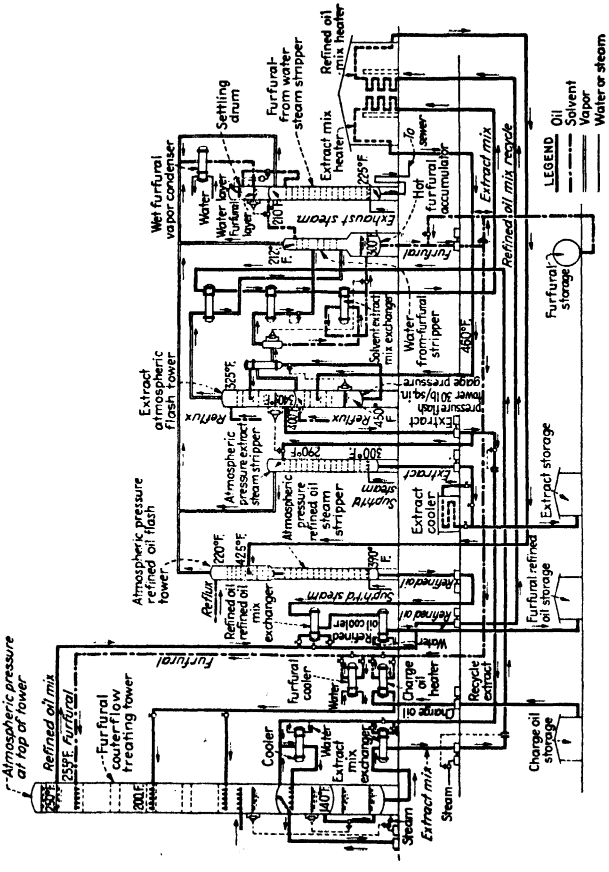

FIG. 184.—Furfural solvent refining plant. (*The Texaco Development Company.*)

varies, but two parts of solvent per part of oil have been used in many operations.

The type of plant is indicated in Fig. 184. Contacting is effected in a countercurrent-flow tower, which may be packed with wood slats. A higher temperature is maintained at the top than at the bottom of the tower, and an enhanced degree of solvent-fractionation is attained thereby. The refined oil mix (raffinate solution) contains so little solvent that it can be purified by heat-exchange and vacuum steam stripping, but the extract solution requires a pipestill and atmospheric flashing as well as vacuum stripping. The furfural-water equilibrium system involves partial insolubility, and the formation of a constant-composition constant-boiling-point mixture at 97.9°C. The mixture contains 34 per cent furfural by weight. At room temperature this mixture separates into a furfural-rich solution containing 96 per cent furfural and a water-rich solution containing 8 per cent furfural. Thus, the constant-boiling mixture is separated into two solutions in the top of the furfural fractionator of Fig. 184—and the furfural-rich solution is freed from water in a separate steam stripper that receives heat from the hot furfural vapor produced in the extract distillation.

The cost of operation[7,10] ranges from 9 to 17 cts. per barrel of oil charged to the plant, and the respective costs[7] are somewhat as follows:

	Per Cent
Operating:	
Labor	21.0
Material, supplies, etc.	1.9
Fuel	28.6
Steam, power, water	28.4
Repair:	
Labor	1.1
Materials and supplies	1.5
Furfural loss	17.5

The installation cost[9] ranges from $200,000 for a 600-bbl. plant to $500,000 for a 3,800-bbl. plant.

Duo-Sol Process.—This is the only double-solvent process which has been used extensively. Two nearly immiscible solvents are employed. One of these (propane) dissolves paraffinic hydrocarbons, and the other (cresylic acid or "Selecto") dissolves naphthenic hydrocarbons. The two solvents are used in a countercurrent system of flow, and the feed is introduced at an intermediate point in the flow system. In one end of the extraction system the outgoing cresylic acid solution is stripped of paraffinic material by pure propane, and in the other end the outgoing propane solution is stripped of naphthenic material by

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[10] SMOLEY, SCHUTTE, and DAVIS, *Oil Gas J.*, Nov. 10, 1938, p. 37.

pure cresylic acid. Thus, a true countercurrent stripping operation is maintained, although the extraction is conducted as a series of countercurrent batch contacting and settling operations. A diagram of the process is shown in Fig. 185. The extractor is not shown in detail. It consists of nine settlers or compartments. The heavy cresylic acid solution is pumped from one compartment to the next, and the propane solution is also pumped; but in a countercurrent manner. The feed is introduced in compartment 3 nearest the end at which propane is introduced.

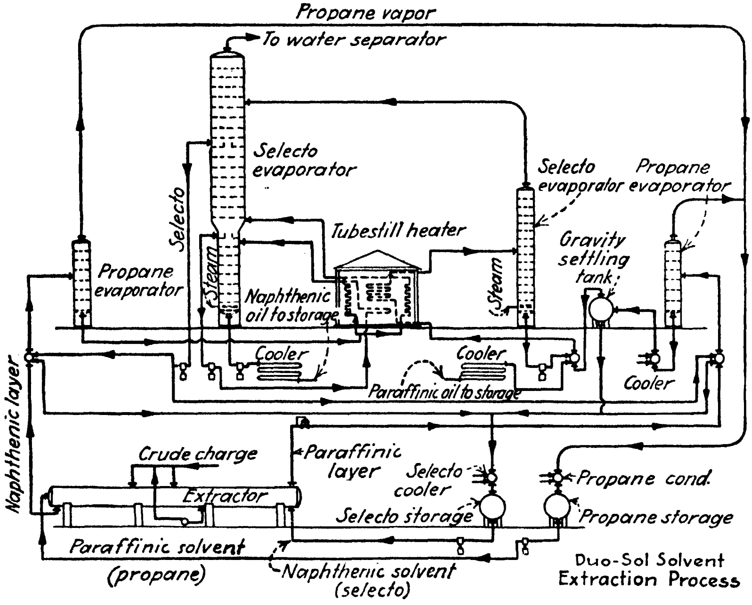

FIG. 185.—Diagram of Duo-Sol process. (*Max B. Miller and Company, Inc.*)

From 125 to 400 per cent "Selecto" (based on charge-stock) is employed, depending upon the stock, and 150 to 400 per cent propane. In general, the naphthenic stocks require more propane, and the paraffinic stocks require more "Selecto."[7] Contacting is accomplished at about 85°F.

The Propane Processes.—Propane assumes significance as a solvent because it is useful in so many ways. It extracts paraffinic hydrocarbons from oil, or inversely it precipitates asphaltic or resinous materials; it is used as one of the solvents in the Duo-Sol process; it is used for dewaxing; and it greatly facilitates

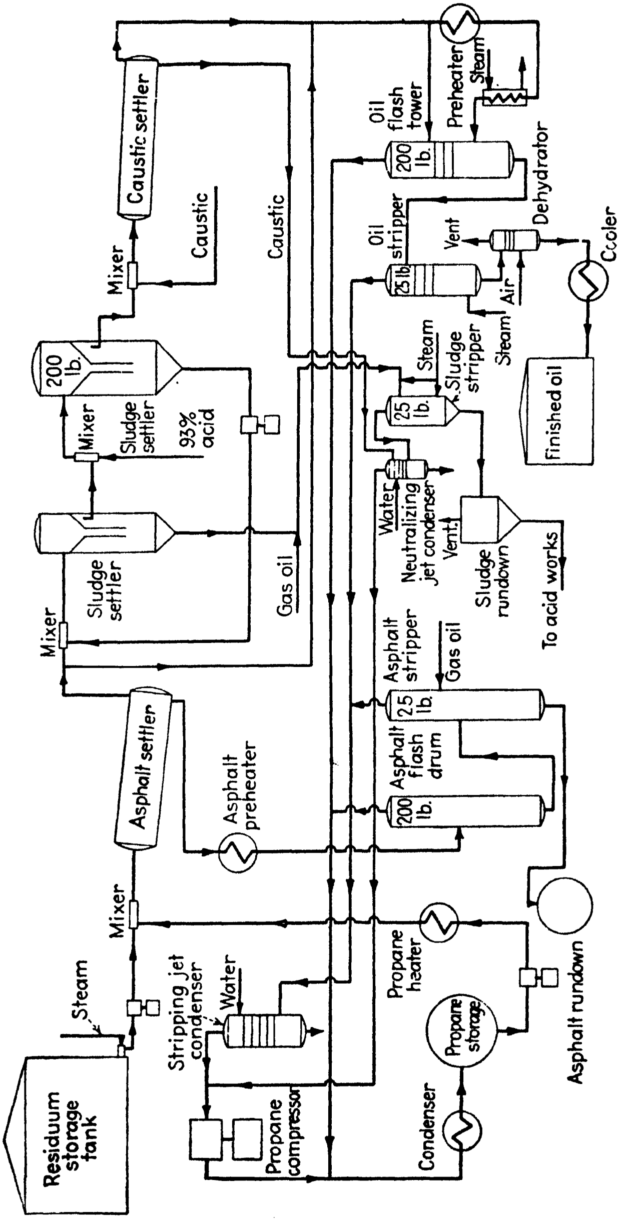

FIG. 186.—Flow diagram of propane deasphaltizing and sulfuric-acid treating in propane solution. (*Oil Gas J.*)

treatment with sulfuric acid. By utilizing a series of these processes, as deasphaltizing followed by acid treating and by dewaxing, it is possible to avoid a number of the costly solvent-removal operations that would be necessary if several different solvents were employed. The low-boiling-point of propane facilitates its separation from high-boiling oils, and refrigeration for dewaxing can be obtained by evaporation of the propane. It is exceedingly fluid, and hence the separation of liquids and wax is simplified. Finally, it is a cheap material, and most of the plant losses can be recovered in the regular gas recovery system.

A system for deasphaltizing and acid treating in propane solution[6] is shown in Fig. 186. This plant was used to process a very heavy mixed-base residuum (18 A.P.I.) for the manufacture of a 32.5 A.P.I. green-cast cylinder stock. The advantages in acid saving, yield, etc., are evident in the following comparison of regular acid treating and the new procedure:

TABLE 100.—UTILITIES, CHEMICALS, AND BY-PRODUCTS OF PROPANE ACID TREATING

Per 100 gal. of unpercolated wax-bearing green-cast stock

	Old procedure	New procedure
Fuel oil, gal	20	None
Steam (live), lb	2,845	1,040
Steam (exhaust), lb	395	365
Electric power, kw.-hr	12	None
Acid, lb	420	40
Caustic, lb	1.5	4.2
Acid sludge, gal	111	21
Asphalt, gal	0	20
Slop oil, gal	1	0
Loss, gal	7.5	0

Deasphaltizing is applied primarily for the separation of small amounts of dark-colored asphaltic materials—and thus may or may not result in an oil product that is a superior lubricating oil, depending upon the characteristics of the raw stock. At 80 to 160°F. propane precipitates asphaltic material in small amounts.[7] The amount of propane used amounts to two to ten times as much as the charge-stock. The process consists simply in mixing the oil and propane and allowing the asphalt to settle. By a series of settlings at increasing temperatures it is possible to precipitate asphalt followed by lighter and lighter petroleum resins.

Other Processes.—Although many other processes deserve attention, particularly the Chlorex,[1] Phenol,[4] and Nitrobenzene[1] processes, space does not permit a discussion of them. The usefulness of the processes discussed in this chapter appear to be well established, particularly by the amount of oil being processed, but all the solvent processes are so new that further research and economic investigations will be necessary in order to establish the relative importance and special advantages of the several processes.

References

Brown, E. E.: Kendall Operates New Solvent Unit, *Oil Gas J.*, Mar. 25, 1937, p. 107.

Cooke, Petty, and Barton: Propane Treatment of Lube Oil Stocks, *Ref. Nat. Gaso. Mfr.*, May, 1938, p. 178.

Gard and Ragatz: Fundamentals of Solvent Refining Operation, *Oil Gas J.*, June 6, 1940, p. 49.

Kalichevsky, Simpson, and Story: Solvent Refining of Lubricating Oils: The Operator's Viewpoint, *Oil Gas J.*, June 3, 1937, p. 88.

Mertens, F. T.: Refining Pennsylvania Oils with Furfural, *Oil Gas J.*, Nov. 7, 1940, p. 47.

CHAPTER XXVIII

DEWAXING

The solid materials that are found in high-boiling petroleum oils can be classified into two general types, *viz.*, crystalline wax and amorphous wax. Crystalline wax is found in wax distillate (paraffin oil), and amorphous wax, or petrolatum, is found in cylinder stock. In reality, both materials are crystalline, but the crystals in the petrolatum stock tend to be small, so that the petrolatum behaves physically as a colloidal or jellylike material. The crystalline nature of all waxes is evident in the several newly developed solvent dewaxing processes. In these the so-called amorphous wax can be successfully collected on filters.

The crystalline wax that is found in wax distillate can be filtered from the oil; but amorphous wax is sticky, and it quickly plugs the pores of a filter cloth.

Composition of Paraffin Wax.—The waxes extend throughout the entire boiling-range of the lubricating oil stocks. Attempts to separate wax from oil by fractionation have met with no success. Buchler and Graves[1] have studied the wax-bearing stocks of Salt Creek, Wyo., crude oil. All of these stocks, paraffin wax, slop wax, petrolatum, and sucker rod wax, were found to consist mainly of the same series of hydrocarbons, and the authors concluded that the waxes consist of the normal paraffin series. They also isolated a material that they call "soft wax," and they attribute the different pressing characteristics of wax stocks to the amount of soft wax that each stock contains. They believe that paraffin distillate contains small amounts of soft wax and that petrolatum stocks contain a large amount. Ferris, Cowles, and Henderson[2] have also made a thorough examination of wax-stocks by the repeated crystallization of high- and low-melting-point waxes. They obtained six different melting-point waxes. Part of each of these waxes came from both high- and low-melting-point wax-stocks, and hence it is clear that some of the same hydrocarbons are present in both high- and low-melting-point waxes. They found no soft wax, as reported by Buchler and Graves. The six waxes ranged in melting-point from 84 to 140°F., and all had approximately the same boiling-point. These authors conclude that petroleum waxes consist mainly of normal paraffin hydrocarbons and that the rest of the material consists of isomeric branch-chain hydrocarbons. Others[3] found small amounts of cyclic compounds in the samples. Clark and Smith[4] studied the wax fractions that were prepared by Ferris and others[2] by X-ray diffraction patterns, and they concluded that the wax consisted of about 65 per cent *n*-paraffin hydrocarbons and at least 20 per cent isoparaffin materials.

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[1] The Petroleum Waxes, *Ind. Eng. Chem.*, **19**, 718 (1927).

[2] Composition of Paraffin Wax, *Ind. Eng. Chem.*, **21**, 1090 (1929).

Crystallization of Wax.—Three theories have been proposed to explain the manner in which wax crystallizes or fails to crystallize. Zaloziecki[5] proposes the proto-pyro-paraffin theory, which states the existence of an amorphous wax that probably consists of branch-chain hydrocarbons. This amorphous material decomposes into a crystalline variety upon heating at mild cracking temperatures. The theory was probably developed because at that time a so-called "cracking distillation" was thought to be necessary if a pressible wax distillate was to be obtained. Gurwitsch[6] suggests that the crystalline behavior of wax-stocks is dependent upon the properties of the crystallizing medium. If the oil is viscous, the crystals will be small and an amorphous wax results; whereas if the oil is fluid, the crystals are large and a pressible type of wax results. In addition, he believed that bituminous or high-boiling materials inhibit the crystallization of wax. It is found that a careful separation of high-boiling asphaltic materials by fractionation does cause the formation of a more crystalline wax. The third theory of wax crystallization, that of Buchler and Graves,[1] has already been discussed. Still others attribute the differences in the waxes to the presence of impurities, perhaps the soft wax of Buchler and Graves,[1] which results in different surface-tension properties.

Perhaps all of the theories outlined above are related, in part, to the crystalline condition that a wax may exhibit. A more complete study of wax crystallization is given on page 635, under the heading of pressibility of wax-stocks.

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[3] Mair and Schicktanz, *Ind. Eng. Chem.*, **28**, 1056 (1936).

[4] *Ind. Eng. Chem.*, **23**, 697 (1931).

[5] *Z. angew. Chem.*, **3**, 126, 318 (1888).

[6] "Scientific Principles of Petroleum Technology," 2nd ed., D. Van Nostrand Company, Inc., New York, 1924.

Three crystalline forms of wax are generally recognized, *viz.*, plate form, needle form, and mal, or imperfect, crystal formations. The plate form of crystal is necessary for good pressing characteristics, but the needle form is necessary for the sweating operation. The plates apparently "roll up," or fold, into the needle type of crystals. Davis and Campbell[7] have studied the crystalline structure of 13 fractions of wax oil. The fractions were obtained by a true-boiling-point distillation of a Mid-Continent wax distillate. The properties of the fractions are given in Table 101.

TABLE 101.—FRACTIONS OF WAX OIL

Fraction No.	Per cent of crude at end of fraction	Universal vis. at 100	Temperature, deg. F., at cut point, approx.		Pour-point, deg. F.	Per cent wax by weight	Melting-point of wax, deg. F.	Crystalline structure
			At 3 mm.	At 760 mm.				
1	58.2	40	358	680	3	0	...	None
2	60.4	51	377	700	35	7.2	96	Few plates
3	62.6	66	402	727	53	9.1	106	Plates
4	64.8	75	420	752	58	9.3	112	Plates
5	67.0	89	442	773	66	7.4	124	Plates
6	69.2	115	460	789	76	10.8	128	Plates
7	71.4	152	478	813	85	10.1	132	Partly malform
8	73.6	200	499	832	89	9.7	137	Partly malform
9	75.8	258	520	862	95	9.2	142	Malform
10	78.0	330	541	886	98	8.7	145	Malform
11	80.2	400	567	915	102	9.5	145	Malform
12	82.4	480	598	950	105	6.8	145	Malform
13	84.6	470	625	978	108	5.2	149	Plates

The clean-cut crystals appearing in fraction 13 were probably due to decomposition during the distillation of the last fraction.

The fractions were blended together as follows: 1 to 6 inclusive, 1 to 7, 1 to 8, etc., including all the cuts. The size of the crystals was progressively smaller and smaller as cuts were added, but with the exception of blends 1 to 12 and 1 to 13 the crystalline size and form were satisfactory. The approximate end-points, at atmospheric pressure, of the blends were as follows: 780, 798, 819, 830, 851, 872°F.; and for the two unsatisfactory blends (1 to

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[7] *Oil Gas J.*, May 25, 1933, p. 49.

12 and 1 to 13), 893 and 921°F. Thus it appears that wax oils having end-points exceeding about 860°F. are not satisfactory, and many refiners have found it advisable to limit the end-point to 835°F. Nevertheless, other factors, such as the characteristics of the oil, the degree of fractionation, the viscosity, and the amount of cracking, doubtless alter the allowable end-point for a pressible stock.

Pressing and Sweating.—Most refiners still (1940) use the pressing and sweating processes for removing and producing wax from wax distillate, but solvent processes are gaining recognition. A mixture of wax and oil, called slack wax, is obtained from the filter presses, and the slack wax is frozen into a cake and allowed to warm slowly so that the oil drains from the cake. Figure 187 shows the general processing scheme for conducting these two operations. Most modern plants, particularly when manufacturing low cold-test oils, use direct expansion of ammonia for chilling the stock, but many older plants circulate brine through the chillers.

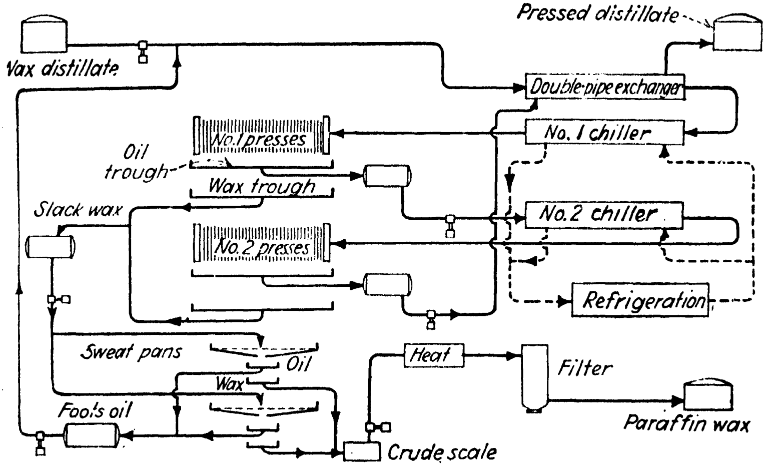

FIG. 187.—Diagram of the operations of pressing and sweating (double pressing).

The double-pipe chilling machine has been adopted almost exclusively for chilling wax oil. This machine is constructed much as a double-pipe cooler except that a revolving-screw or ribbon-type conveyor turns in the inner pipe. The conveyor scrapes the congealed wax from the walls of the pipe and moves it through the machine. The common size of chiller has a 6-in.-diameter inside pipe and an 8-in.-diameter outside pipe. The chilling machine is built of several sections or lengths of pipe arranged in stacks usually five to eight sections high. The conveyors for each stack (or for two stacks) are actuated by a common chain drive. Thus 24 sections of chiller can be arranged in four stacks, each stack 6 sections high, and with two chain drives. Sometimes the conveyors are actuated by a single motor so that if one section should freeze or plug, the large motor will have sufficient power to break the wax in the frozen section. However, this practice often causes damage to the machine, and it is usually necessary to take a frozen chiller out of service and warm it.

The rate of cooling is greatly dependent upon the effectiveness of the scrapers, particularly the amount of mixing that occurs. If the scraper fits poorly, the rate of heat-transfer drops to the low values of 2 or 3 B.t.u. per square foot per degree Fahrenheit per hour. With closely fitting scrapers that mix the wax into the oil, rates of 16 B.t.u. have been recorded. Commonly accepted values of the transfer rate are:

Type conveyor	Cooling conditions	Transfer rate, (B.t.u.)/(deg. F. diff.) (sq. ft.) (hr.)
Screw	Brine circulation	4–5
Screw	Direct expansion	7–10
Ribbon	Direct expansion, nonturbulent flow	8–12
Ribbon	Direct expansion, turbulent flow, and recirculation	15

Thus a section of chiller having a surface of 55 sq. ft. will be able to cool 12 to 18 bbl. of wax oil per day through the customary range in temperature. The higher capacity is for chilling the oil to 10 to 15°F. when some heat-exchange is used, and the lower capacity is for cooling to 15°F. without exchangers or to 0° with exchangers. Manufacturers of refrigeration equipment should be consulted concerning an actual installation.

Two kinds of plates are used for filtering the chilled wax oil. One is a recess type of plate (permanent ring), and the other

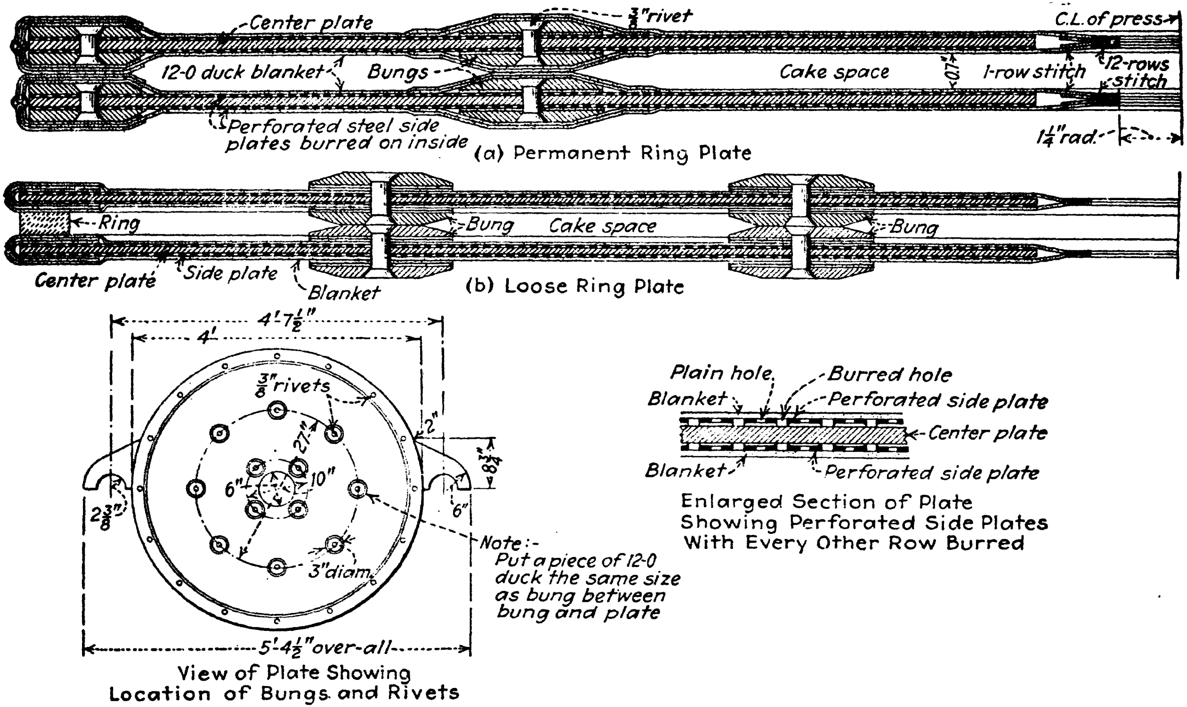

FIG. 188.—Details of filter plates. (*a*) Permanent-ring type; (*b*) loose-ring type. (*Carbondale Machine Company.*)

consists of a flat plate and a spacer ring (loose-ring type) (Fig. 188). It is claimed that the blanket on the permanent ring plate is worn by the tool that is used to pry the plates apart. The loose-ring plate is less expensive, but the riveted spreaders must be removed each time that the canvas is replaced, and many refiners feel that the ring involves needless handling. Plates are manufactured in diameters of 27, 36, and 48 in., but the 48-in. plate is used almost exclusively. Each plate has a hole in the center which allows the chilled oil to flow through the entire length of the press to every plate. Special canvas (12-0) filter cloth is sewed around each plate, and in the loose-ring type the "blanket" is also fastened to the plate by riveted spreaders. The wax remains on the cloth, and the oil flows down the plate and around the edge of the plate to the bottom. The pressure at the end of the pressing operation seldom exceeds 450 lb. per square inch, and the common "drying-off" pressure is 350 lb. Ten or twelve plates require a foot of length, and the presses are normally assembled with 250 to 500 plates in a press. The capacity of the press is greatly dependent on the properties of the wax oil, such as the wax content, the crystal structure, and the pressing temperature (page 636). For a normal stock that contains 5 to 8 per cent wax and for single-pressing operation, one or two 48-in. plates are required for each barrel of Pennsylvania oil that is pressed per day and two or three plates for a Mid-Continent oil. Even lower capacities are common with double-pressing operation or if the stock contains a large amount of wax. The amount of slack wax that is obtained from the presses is far greater than the 5 to 8 per cent finished wax and may in some cases amount to 30 per cent of the wax distillate.

Low-pour-point oils are becoming more and more common. These oils require a low pressing temperature, and the rate of filtration is much slower. In general, the stock should be chilled to 5 to 10°F. below the desired pour-point for single-pressing operation, but for a double-pressing operation the stock need not be chilled to such a low temperature. One refiner reports that zero-pour-point oils can be obtained by pressing at +5°F., and another reports a temperature of −8°F. The difference doubtless arises because of differences in the fractionation of the stocks and in the crystalline condition. Direct expansion of ammonia is advantageous for the obtainment of these low temperatures.

When brine is used as the cooling medium, two temperature differences are involved and the ammonia temperature must be much lower than when direct expansion is used.

The operation of *sweating* consists of cooling the slack wax to a congealed mass and slowly heating it to temperatures of 100 to 140°F. The wax is heated in long shallow pans, usually about 10 ft. wide, 40 or 50 ft. long, and sufficiently deep to hold a 5- to 7-in. cake of wax. A flat perforated metal sheet or a 50-mesh screen lies across the bottom of the pan. A pipe coil for cooling and heating lies just above the screen. The pans are arranged, one above another, in stacks of about eight and housed in a building or oven. The oven has steam coils along the walls to aid in maintaining uniform temperature conditions within the oven.

Fig. 189.—"Spudding" a wax press. (*Carbondale Machine Company.*)

In conducting a sweating operation, cold water is turned into the pans up to the screen and circulated through the coils above it, and slack wax is pumped into the pan. The wax solidifies into a cake, and the water is withdrawn, leaving the cake on the screen. The temperature is then gradually increased by circulating warmer and warmer water through the coils in the cake and by passing steam through the coils on the walls of the oven. If the wax is in the proper condition, it gathers into well-defined needle crystals, and the oil sweats or drips from the wax cake. The oil is called foots oil, and it may be returned directly to the wax distillate or it may be resweated for the recovery of additional wax and a less waxy foots oil. Often the oil from the wax cake is collected in two portions, the first, foots oil, and the second, *intermediate wax.* In making 118°F. melting-point wax, the intermediate wax may be resweated with the slack wax, but more frequently it is sweated separately. The intermediate wax from a high-melting-point sweating operation often contains as much as 50 per cent slack wax. The resweating of intermediate wax can be economically conducted in a tank that contains several layers of water coils, because the wax sweats well and a very thick cake is possible. Very low-melting-point waxes are usually made by resweating the foots oil.

The rate of heating is greatly dependent on the uniformity of temperature within the cake. With circulating water as the main heating medium, the total time for the sweating cycle is about 30 or 40 hr. The exact time depends upon the melting-point of the wax that is being produced, the crystalline characteristics, and the uniformity of temperature throughout the cake. For 110 to 112°F. melting-point wax, only 24 to 36 hr. are required, but for 120°F. wax the time is 35 to 45 hr. The use of automatic temperature-control instruments is an advantage in maintaining a uniform cycle of heating.

The total time for the sweating cycle is not proportional to the melting-point of the wax because about 16 hr. is required for the charging, cooling, and melting operations. The melting-point of the crude scale wax is about the same as the maximum temperature attained in the sweating operation. The resweating of intermediate wax does not take so long because the cake is more porous. L. D. Wyant[8] has made a systematic study of wax sweating. He concludes:

1. Super chilling the wax cake before starting to sweat does not increase the yield or quality of wax produced.
2. Extremely slow chilling allows or causes paraffin wax to segregate into patches or blocks throughout the slack wax cake.
3. In chilling a wax cake before starting it to sweating, all the material should be chilled to at least a complete semi-solid mass; however, additional chilling is a loss of time in cycling.[9]

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[8] Separation of Wax from Distillate, *Oil Gas J.*, Oct. 2, 1924, p. 224.

[9] Author's note: Most refiners find that the wax cheese must be perfectly solid before starting the sweating operation or the yields are poor.

4. No advantage compatible with the cost is gained by extremely rapid chilling.
5. Local overheating, if of only a few (2 or 3) degrees difference, has an appreciable effect on a sweating wax cake.
6. Water coils arranged so heated water can circulate through the sweating wax cake decreases the cycling time required for sweating.

In a study of the recovery of wax that was obtained by several Mid-Continent refiners, he found that the recovery of wax varied greatly. The efficiency of the sweating operation ranged from 23 to 85 per cent and averaged about 50 per cent. Donnell and Burch[10] find that slack waxes containing more than 50 per cent oil yield little crude scale whereas at 20 per cent oil the yield of scale is 52 per cent.

The crude scale has a slightly yellow color. This discoloration may be removed by treating the molten wax with acid (or sometimes dilute caustic solution) in an agitator, but filtration through fuller's earth is all that is normally required.

Pressibility of Wax Stocks.—The rate at which wax stocks can be pressed is of prime importance to the refiner. By slight changes in the operating conditions, a wax distillate may be produced that presses very slowly or cannot be pressed at all.

Some factors that affect the pressibility of a wax oil are

1. Viscosity.
2. Fractionation.
3. Distillation range.
4. Wax content.
5. Crystal structure.
6. Extent of cracking.

Viscosity.—The pressing qualities of wax oils from the same crude oil are somewhat dependent on the viscosity. The higher the viscosity the slower the rate of pressing. Wax oils that are pressed without dilution usually have a viscosity between 55 and 75 sec. Saybolt at 100°F. Higher viscosity oils[11] have been pressed, but usually they are diluted with heavy naphtha to a viscosity of about 60 sec. The use of naphtha permits single-pressing for stocks that would otherwise require double-pressing.

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[10] Experimental Control . . . Sweating, *Ref. Nat. Gaso. Mfr.*, November, 1938, p. 603.

[11] A 110 viscosity distillate is being pressed without dilution by one company.

The viscosity at the pressing temperature is of more interest than the viscosity at 100°F. Davis and Campbell[7] report viscosities at the pressing temperature of 1,200 to 2,100 sec. (Table 102).

The pressing qualities of a distillate are also dependent on other factors than the viscosity, so that the several factors must be considered collectively. The proper viscosity for a particular distillate must be determined in the plant by a consideration of the several factors and by conducting plant experiments.

TABLE 102.—PRESSING TESTS

Pressing stock No.	1	2	3	4	5	6		7
Gravity, A.P.I.	34.2	32	31	31.4	31.7	31.6		
Flash-point, deg. F.	90	170	360	280	320	315		
Viscosity of distillate at 100°F.	63	70	94	66	68	75		100
Cold test, deg. F.	66	68	74	42	56	80		
Distillation-range at 40 mm., deg. F.								
Initial boiling-point	....	256	450	256	312	306		
10 per cent	344	312	476	395	394	416		
20	466	350	493	416	426	445		
30	494	473	509	436	453	469		
40	511	498	525	461	479	491		
50	527	518	541	490	503	513		
60	544	539	557	524	523	533		
70	564	561	573	557	543	554		
80	588	585	593	590	562	580		
90	622	611	615	625	590	616		
End-point	648	632	637	643	625	652		
End-point, 760 mm. approx	862	844	849	859	835	870		
Wax content, per cent	8.75	6.75	7.66	1.58	5.77	4.8		
Melting-point of wax, deg. F.	118	123	123	119	124	123		
Per cent raw 200 vis. neutral	50	48	50	51	33	39		
Pressing characteristics:								
Pressing temp.	−18	−8	−10	−5	−6	+8	−5	15
Vis. at 100°F.:								
Distillate	63	70	94	66	68	75	75	100
Pressing stock	55	70	58	66	68	75	66	100
Dewaxed oil	57	76	63	68	74	82	69	114
Viscosity at pressing temp. approx	1,400	2,100	1,350	1,380	1,800	1,200	1,400	1,800
Pressing rate, bbl. per plate per day	0.43	0.43	0.41	0.4	0.37	0.35	0.3	0.45
Fractionation	....	....	....	....	Poor	Poor		
Crystal formation	Good	Good	Good	Fair	Poorly formed	Very small		

Fractionation.—The degree of fractionation plays an important part in the pressing qualities of an oil.[12] The quantity of material boiling above 800°F., and particularly the "tail" of poorly fractionated material in the oil, affects the pressing rate greatly. A poorly fractionated stock may press more slowly than a well-fractionated product that has a much higher end-point because of minute quantities of very high-boiling material. Dunmire[12] concludes that fractionation is more necessary in producing a pressible distillate than cracking. Fractionation also affects the centrifuging properties of the cylinder stock, and hence a poor separation between the cylinder stock and the wax distillate results in trouble with both of these stocks. For this reason refiners have sometimes found it necessary to take a "slop" wax cut between these two stocks.

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[12] DUNMIRE, H. J., *Nat. Petroleum News*, Apr. 23, 1930, p. 38.

Distillation-range.—This constitutes a valuable method for the laboratory control of the pressing operation. A common method of determining the boiling-range is by the Bureau of Mines vacuum distillation operated at 40 mm. pressure. End-points at 40 mm. pressure of 610 to 640°F. are possible without spoiling the pressibility of the stock. This corresponds to a cut-point of about 840 to 870°F. (atmospheric pressure) on the true-boiling-point distillation curve.[13] It appears that the viscosity of the heaviest part of the wax distillate also affects the pressibility. In general, it should not exceed about 580 sec. at 100°F.

Wax Content.—An abnormally high wax content usually lowers the pressing rate because the presses must be dumped oftener. At the same time, the wax in the higher wax-content oils often crystallizes better, so that pressing may actually be facilitated in spite of the high wax content. A method of determining the wax content is given by Davis.[7] The average wax content of distillates is about 6 per cent; but some stocks contain as little as 1 per cent wax, and others contain as much as 25 per cent.

Crystal Structure.—The crystal structure is perhaps the most important factor that affects the pressibility of a stock, but it is related and dependent on the several other factors that are discussed herein. A means of examining and photographing waxes is described by Davis.[7] Figure 190 shows several characteristic photomicrographs of wax distillate. A stock having very good pressing properties is shown in Fig. 190*a*; a typical stock in *b*; a stock with too high an end-point in *c*; and one that indicates that a small amount of crude oil had leaked into the stock during heat-exchange in *d*. The size of the crystals shown in the figure is of little significance unless they were grown under comparable conditions, because the size depends upon the length of time that they are allowed to grow before the picture is taken.

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[13] If the wax oil is cracked before pressing, the cut-point may be 30 to 40° higher, but the cracking distillation of wax oils is expensive, involves losses of oil, and is no longer widely practiced.

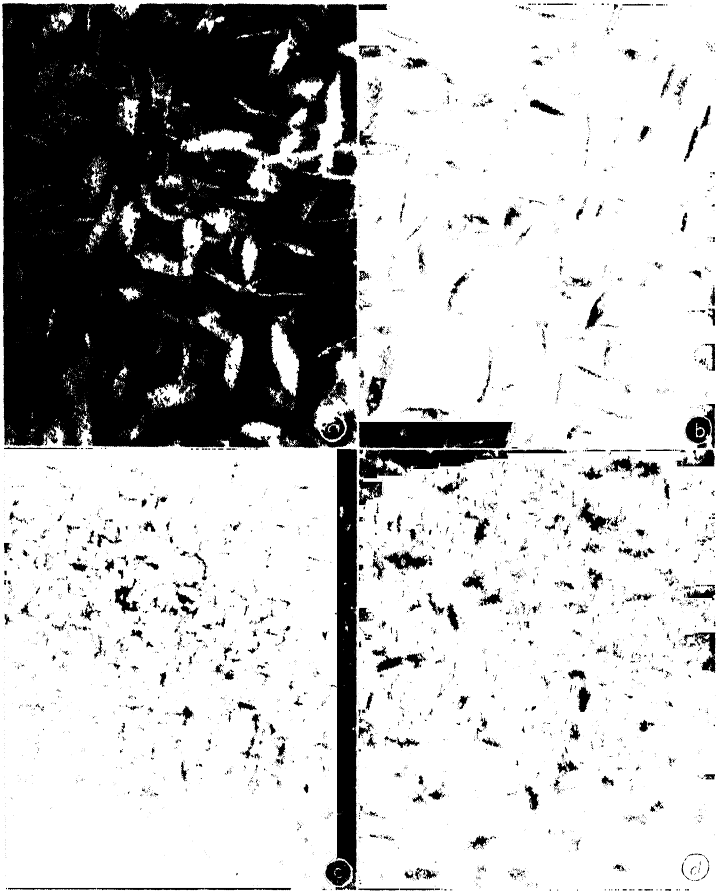

Fig. 190.—Photomicrographs of wax: (*a*) very good; (*b*) typical; (*c*) high end-point; (*d*) crude oil leaked into distillate in exchanger. (*L. L. Davis, Continental Oil Company.*)

Cracking Distillation.—Until recently, all refiners prepared their wax-stocks for pressing by a so-called "cracking distillation." The wax oil was heated for several hours at about 800°F. The wax crystallizes more cleanly from a stock handled in this manner; but a loss of lubricating oil occurs, and the operation is expensive. Dunmire[12] finds that greater yields of pressible distillate are obtained by cracking the distillate but that an even larger yield is obtained by carefully fractionating the stock. During the last 10 years it has been definitely proved that cracking is not necessary in order to produce a pressible distillate. If other factors such as fractionation, viscosity, boiling-range, and crystal structure are satisfactory, the stock will be pressible without a cracking distillation.

In determining the suitability of a stock for pressing, all of the foregoing factors must be considered collectively. In the control of plant pressing operations, the wax oil should be examined for at least the following characteristics: (1) viscosity, (2) boiling-range at 40 mm. pressure, and (3) crystal structure.

Cold Settling and Centrifuging.—These processes have been widely used for the dewaxing of cylinder stock, but solvent processes are now claiming attention. The *cold-settling* process was an outgrowth of the experiences of the early Pennsylvania refiners. They allowed their crude oil to stand through the winter in storage tanks. During cold weather, the wax separated and settled to the bottom of the tank so that a partially dewaxed crude oil could be drawn from the top of the tank. The cold-settling process involves the use of large well-insulated settling tanks. Brine coils are suspended in the tanks, and by slowly cooling the cylinder-stock solution (60 to 70 per cent naphtha) the wax collects and settles to the bottom of the tank. The lowest economical pour-point by this process is about 30°F., and hence the process has been gradually abandoned. However, slow-cooling tanks similar to settling tanks, except that they are used continuously, are used in cooling the solution for the centrifuge process.

The *centrifuge* process of dewaxing is now widely used. The process is illustrated in Fig. 191. The percolated cylinder-stock solution, containing about 65 per cent naphtha, is continuously chilled in slow-cooling tanks to about 10°F.; and if low-pour-point oils are required, the cooling is continued in chilling tanks that are provided with mixing paddles. The latter tanks are usually cooled by direct expansion of ammonia. The rate of cooling in the slow-chilling tanks should be about 3 or 4° per hour, but a more rapid rate of cooling is usually possible after a temperature of 0° has been attained. The temperature difference between the solution and the cooling medium must be kept to less than about 20° in the slow-chilling tanks in order to avoid fouling of the transfer surfaces. If pour-points of 20 to 30°F. are satisfactory, the oil should be cooled to about −10°F. and direct expansion of ammonia is not necessary. For zero-pour-point oils the chilling must be continued to about −45°F., and for some stocks a temperature of −55°F. may be necessary. The chilled solution is charged to Sharples centrifuges through a constant-head feed device. The centrifugal force separates the wax and oil: the oil from the top and center of the bowl and the wax from a point lower. Figure 192 shows the arrangement at the top of the machine. A stream of warm water (150 to 180°F.) sprays on the petrolatum to prevent freezing the wax in the bowl. The dewaxed solution flows directly to storage, but the wax solution is separated from the carrier-water in a separator tank. In modern plants it is becoming common practice to use the cold dewaxed oil as the cooling agent in the slow-chilling tanks. In so doing it is sometimes necessary to recirculate some warm dewaxed oil to maintain the proper temperature differential between the two stocks.

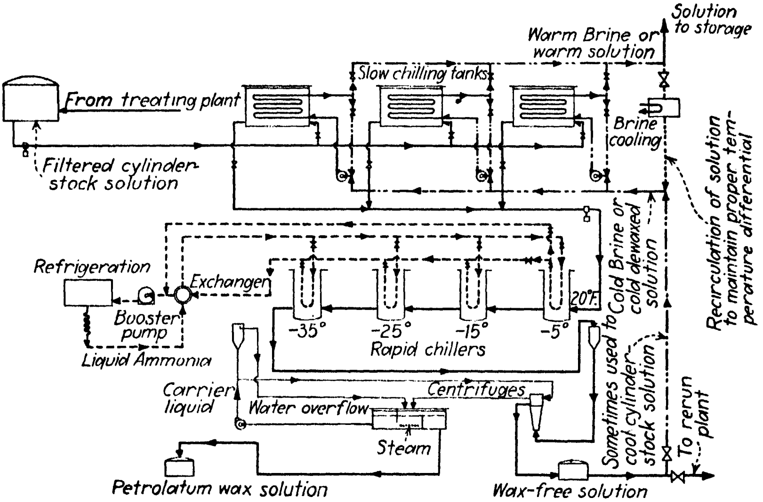

FIG. 191.—Centrifuge process for dewaxing cylinder stock.

The capacity of the Sharples machine is 25 to 45 bbl. per day based on cylinder stock. Thus each machine handles 70 to 180 bbl. per day of solution, depending upon the pour-point of the finished product, the properties of the stock, and the amount of dilution. The machine operates at 17,000 to 19,000 r.p.m. and requires about 1 kw. per hour of power. The refrigeration requirement per machine per day is 5 to 8 tons.

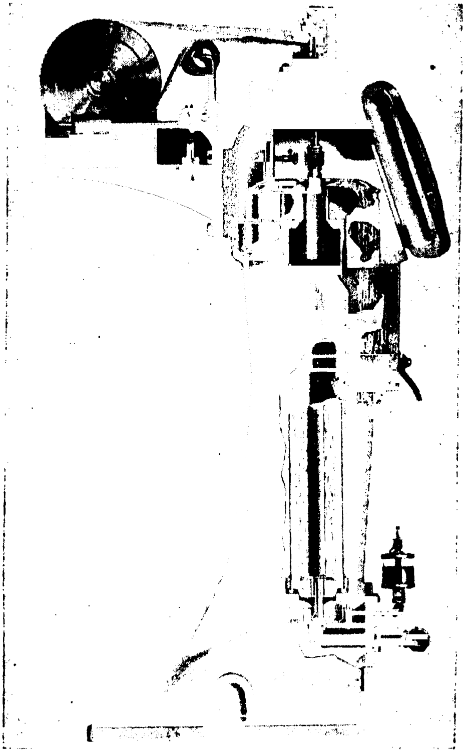

FIG. 192.—Sharples Super-Centrifuge for dewaxing cylinder stock solution. (*Sharples Specialty Company.*)

The secret of successful centrifuge operation is the maintenance of uniform operating conditions in the entire plant operation as well as the operation of the centrifuge plant. The stock must be carefully fractionated in the topping or vacuum distillations to eliminate crystalline wax. The rate of chilling should be sufficiently fast to prevent the formation of large crystals, but too fast a rate of chilling will give a petrolatum that is too colloidal to centrifuge properly. High-boiling dark-colored or asphaltic materials inhibit the growth of crystals, and a stock whose color is lighter than 1⅛ Tag Robinson will probably give trouble. Some refiners have even added colloidal matter to a distilled cylinder stock to inhibit the growth of crystalline wax. The chilling surfaces must be kept free from wax, and the equipment should be designed so that masses of wax cannot accumulate on cooling surfaces, tank bottoms, or lines. A sufficient amount of naphtha must be used to obtain a nonviscous solution at the centrifuging temperature. A solution containing about 70 per cent naphtha and having a gravity of 44 to 47 is usually satisfactory for producing zero-pour-point oil. In producing very low-pour-point oils it may be necessary to use even more naphtha. In the past, the viscosity of the cylinder stock that could be successfully centrifuged was about 110 sec. at 210°F., but by careful operation it is now possible to operate on a stock whose viscosity is as low as 75 sec. at 210°F. This permits most of the wax distillate to be incorporated in the long residuum cylinder stock.

In order to get proper centrifuging properties, many recirculation schemes have been used. In processing very waxy stocks and some overhead stocks, it is necessary to recirculate some of the dewaxed oil. Other stocks can be centrifuged most successfully by recirculating some petrolatum, and in rare cases it has been necessary to add dark-colored material to the stock.

NEW DEWAXING METHODS

The use of two dewaxing methods, *i.e.*, pressing and centrifuging, has been a source of great expense to refiners. In an effort to lower this expense, much attention is being given to the development of methods by which the entire range of wax-bearing stocks can be dewaxed by a single process. Two general types of processes are being studied. In one of these the combined wax distillate and cylinder stock is pressed or filtered, and in the other the entire wax-stock is dewaxed in a centrifuge. With the exception of the filter aid process, all of the proposed processes require the use of a special solvent. The filter aid process relies upon the use of a filter aid material that strengthens and reinforces the wax cake and at the same time keeps it in a porous condition. For those processes which involve filtration, the trend is toward the use of suspended-leaf types of presses, such as the Kelly, Vallez, and Sweetland, rather than the familiar plate-and-frame type that is used in pressing wax distillate. Closed filtering systems are required because the solvents must be recovered or the operation will be an economic failure. In fact, the recovery of the solvent has been a great hindrance to the adoption of new dewaxing methods, and no such process can be highly successful unless the solvent can be effectively recovered and is relatively cheap.

The use of a single dewaxing process for both the high- and low-viscosity wax-stocks has many advantages. The cuts that must be produced in a vacuum-tower are reduced to gas oil, a lubricating oil stock, and tar; only one type of dewaxing equipment is required; only one rerunning operation is necessary; and the production of several blending stocks will be unnecessary. Lower and lower viscosity stocks are being successfully handled by the centrifuge process, but the dewaxing is not entirely satisfactory because of the high cloud-points of the neutral oils.

A number of processes[14,15,16,17] have been used, but the main bulk of oil is now handled in methyl-ethyl ketone plants and propane plants.

Propane Self-refrigeration Process.—Propane dewaxing is usually combined with deasphaltizing[18] because an improvement in color can be attained at little extra cost. The propane dewaxing process is unique because part of the solvent is allowed to evaporate and the entire material is chilled by the refrigeration effect of the evaporation. The advantages of the process are

1. Self-refrigeration.
2. Rapid rates of chilling. The entire operation of filling, evaporating, and emptying the chilling vessel requires only about 90 min.
3. Ability to handle all kinds of wax-bearing stocks.
4. High rates of filtration even for viscous oils.
5. A cheap solvent which may be recovered in the regular gas recovery system of the refinery. The make-up solvent requires only a wash with caustic to sweeten it.

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[14] *Filter aid,* GEE, W. P., *Ref. Nat. Gaso. Mfr.*, June, 1933, p. 238.

[15] *Acetone-benzene,* GOVERS and BRYANT, *Ref. Nat. Gaso. Mfr.*, June, 1933, p. 222.

[16] *Trichlorethylene,* PESTER, C. F., *Oil Gas J.*, May 25, 1933, p. 52.

[17] *Bari-Sol,* ALBRIGHT, J. C., *Ref. Nat. Gaso. Mfr.*, August, 1936, p. 287.

[18] WILSON, KEITH, JR., and HAYLETT, *Ind. Eng. Chem.*, **28**, 1065 (1936).

A simplified diagram[19] of the process is shown in Fig. 193. The wax-stock is dissolved, under pressure, in propane (or butane) in the storage tanks *D* by heating to about 130°F. The solution is then allowed to evaporate and chill itself in the vessels *G* by reducing the pressure to about 50 lb. per square inch. Chilling can be conducted at the rate of 3°F. per minute, and the final temperature is about −40°F. The chilling uses about half of the solution. The chilled solution is pumped to the filters *J*, and it can be filtered at the rate of 2 gal. of solution per square foot of filter area per hour for a solution containing 17 per cent oil and at a rate of 0.8 gal. per hour for a 35 per cent solution. Heavy stocks seem to filter at about the same rate as light stocks. The solvent that remains in the wax and oil is distilled and fractionated under pressure. Steam may be used for heating the solution. It is usually necessary to add additional propane after the chilling operation to keep the proper ratio between oil and solvent.

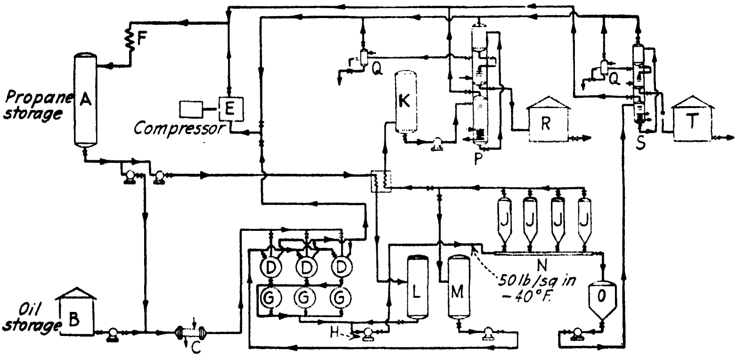

Fig. 193.—Propane dewaxing process. (*Standard Oil Company of Indiana.*)

Recent plants[20] utilize a continuous Oliver-type filter.[21] The press is enclosed to avoid evaporation of propane. The drum of the filter rotates at the rate of 3 to 11 min. per revolution, dipping into a vat of chilled propane-oil slurry. A pressure differential of 2 to 10 lb. per square inch is maintained across the filter cloth. In the vapor space the wax cake during rotation is washed with propane, dried by suction, loosened by a blow-back of high-pressure gas, and scraped into a conveyor. Nozzles for washing the filter cloth with hot naphtha are also provided.

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[19] Bahlke, Giles, and Adams, *Ref. Nat. Gaso. Mfr.*, June, 1933, p. 229.

[20] Anderson, Forrest, and Van Horn, *Nat. Petroleum News*, May 20, 1936, p. 49.

[21] Badger and McCabe, "Elements of Chemical Engineering," McGraw-Hill Book Company, Inc., New York, 1936.

Ketone Dewaxing.—This process is a development of the benzene-acetone process[15] by the use of various mixed solvents consisting of benzene, toluene, methyl-ethyl ketone, methyl-*n*-propyl ketone, methyl-*n*-butyl ketone, or mixtures of these ketones.[22] The advantages of the lower molecular-weight ketones are high filter rates and low solubility of wax, but they have higher vapor-pressures and are somewhat soluble in water.

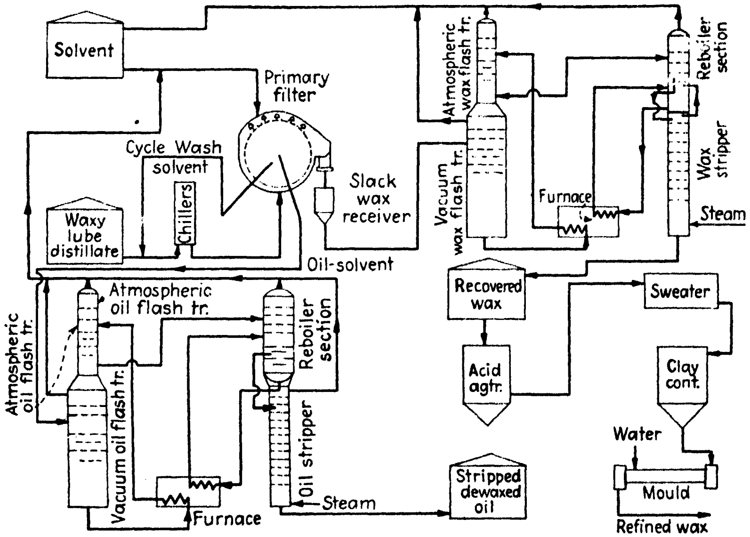

Fig. 194.—Flow diagram of Mixed Ketone solvent dewaxing process. (*Oil Gas J.*)

The wax distillate is diluted with about 2.5 parts of solvent and chilled to the desired pour-point temperature (or even 10° higher). Chilling is first rapid, but final chilling is conducted at a rate of 1 to 2°F. per minute. The chilled mixture is filtered in a continuous rotary filter[21] under a blanket of carbon dioxide. In the Mixed Ketone process[23] shown in Fig. 194 the cold filtrate is first utilized (in series with cycle wash solvent) in the exchanger system for "controlled" chilling. It is then stripped of solvent in a two-stage atmospheric, vacuum, and steam-solvent recovery system. As the filter rotates, the cake is washed with fresh solvent. The slack wax is stripped of solvent and is then acid treated, sweated, and clay contacted. Operating conditions[23] for one plant are:

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[22] Porkorny and Stratford, *Oil Gas J.*, Mar. 31, 1938, p. 96.

[23] Mueller, A. J., *Oil Gas J.*, Apr. 18, 1940, p. 54.

	Paraffin distillate	Light motor oil	Intermediate motor oil	Heavy motor oil
Viscosity, Saybolt Universal	150 at 100	250 at 100	77 at 210	205 at 210
Ratio, solvent to oil	1.9:1	1.7:1	2.2:1	3.2:1
Filtering:				
Temperature, deg. F	20	12	16	25
Gal. dewaxed oil per sq. ft. per hr	6.0	6.3	4.2	2.8
Dewaxed oil:				
Yield, per cent	89	90	91	92
Viscosity	170 at 100	305 at 100	86 at 210	230 at 210
Pour point, deg. F.*	20	5	0	25
Ketone, per cent	0.001	0.003	0.003	0.002
Wax:				
Yield, per cent	11	10	9	8
Oil, per cent	7	5	8	12
Ketone, per cent	0	0	0.001	0.001

* The solid point was 5°F. lower than the pour point in each of these operations.

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CHAPTER XXIX

ECONOMICS OF DESIGN

The economic feasibility of a processing operation is a factor that cannot be overlooked by the engineer. The most sound and exact processing plan may be absurd from an economic standpoint. To a large extent the practicing engineer soon becomes a businessman because of his constant association with economic problems. Perhaps this accounts for the large proportion of engineers who are found in executive positions. The engineer differs from the student of pure science because he is frequently called upon to make decisions on technical matters that have not yet been thoroughly studied.

Economics enters into every detail of design, and hence it will be impossible to illustrate more than a few cases.

COSTS OF PROCESSING

Inasmuch as the operating costs vary widely from plant to plant, no exact data can be presented. Two plants that are operated with the same care and judgment may vary in operating costs as much as 100 per cent. The reason for such differences is easily understood when the following items are considered:

1. Ease of chemical treatment—kind of crude oil.
2. The design of the plant—modern or obsolete.
3. Location—cost of fuel and cost of labor.

These factors explain the wide variation in the operating costs appearing hereafter. The data were taken from actual plant records[1] for a number of plants in all parts of the country. The costs for sales, advertising, general administration expense, depreciation and taxes, and cost of charge-stock are not included.

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[1] The author is indebted to Dr. Sidney Born of the University of Tulsa. Many of the plant records were supplied by him. Date of records, 1927–1932.

All direct charges, such as direct refinery supervision, power, fuel, and materials, are included.

OVER-ALL REFINING COSTS

Direct cost of refining, not including sales, administration, depreciation, and taxes

Operation	Cts. per Bbl. of Crude
Topping	5–19
Topping and cracking, separate	23–36
Topping and cracking, combination	18–29
Complete	24–51

An analysis of these costs by departments is helpful:

Department	Skimming and cracking, cts. per bbl. of crude	Complete, cts. per bbl. of crude
Simple distillation	3.3	6.2
Cracking distillation	17.2	10.4
Gasoline recovery	0.7	0.4
Oil treating—agitators, sludge, handling, etc	1.5	3.8
Filtering and burning clay	....	4.6
Wax handling	....	2.5
Compounding and grease mfg	....	0.8
Boiler house	3.3	5.2
Miscellaneous	4.3	6.3
Total cost per bbl. of crude	30.3	40.2

For a topping and cracking operation in the Mid-Continent area:[2]

	Cts. per Bbl.
Plant fuel	9.0
Labor	5.7
Depreciation and obsolescence	12.0
Royalty (cracking)	7.0
Maintenance	1.5
Treating	0.8
Total	36.0

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[2] WILLSON, C. O., *Oil Gas J.*, Aug. 4, 1932, p. 8.

Miscellaneous Operating Costs and Factors

	Per Cent
Losses:	
Topping distillation	0.7–1.7
Pressure gasoline treating	0.3–4.0
Gasoline, straight-run, treating	0.2–1.0
Kerosene treating	0.2–1.0
Solvents, in treating	0.2–0.5
	Cts. per Bbl.
Distillation:	
Cracking, complete	45–80
Stripping rich absorption oil	1.2–5.5
Stabilizing natural gasoline	4–9
Rerunning pressure distillate	2–8
Treating light oils:	
Acid treating, complete	1.7–4.5
Sweetening, doctor	0.8–3
Sweetening, copper	0.7–1
Clay, vapor-phase	0.5–1.2
Sulfur dioxide extraction	4.6–5.5
Inhibitor, material only	0.15–1.0
Tetraethyl lead fluid, material only	6–32

The costs for processing heavy oils such as neutral oils and cylinder stock are even less consistent. The great variation in these costs is due to the inherent differences in lubricating oil stocks and the variety of treating and dewaxing operations that must be used. Some stocks require five times as much acid as others.

Heavy oils:	
Rerunning complete	4.1–6.2 cts. per bbl. charge
Acid treating complete	11–43 cts. per bbl. treated
Loss in acid treating	
Nonviscous neutral	2.8–4.9 per cent
Viscous neutral	3.5–12.0 per cent
Residual cylinder stock	18.5–40 per cent
Overhead cylinder stock	11–18 per cent
Percolation:	
Nonviscous neutral	7.2–36.2 cts. per bbl.
Viscous neutral	15.4–48 cts. per bbl.
Wax	19.4–36.4 cts. per bbl.
Average of straight filtering	18.4–46.4 cts. per bbl.
Solution filtering	27–75 cts. per bbl. of stock
Clay contacting	35–75 cts. per bbl. charge
Clay:	
Contact clay	$50 per ton
Steaming, discharge and loading	$5 per ton

Burning, wedge-type burner	$1.22–$4.13 per ton
Burning, rotary-type burner	$0.50–$0.92 per ton
Loss during burning	1.5–2 per cent
Dewaxing:	
Pressing and sweating	13.6–46.8 cts. per bbl. wax distillate
Sweating	41.7–125 cts. per bbl. sweated wax
Barreling and molding wax	7.6–106 cts. per bbl. finished wax
Centrifuging	31.9–164 cts. per bbl. brightstock
Refrigeration	46.3–316 cts. per ton of refrigeration
Solvent refining:	
Furfural	9–20 cts. per bbl.
Propane dewaxing and deresining	32–40 cts. per bbl.
Benzene-ketone dewaxing	21–27 cts. per bbl.

The hourly wage rate for labor was 97 cts. per hour in 1938. Various power, steam, and heat costs are

Steam generation:	
Live steam	15.6–30.5 cts. per thousand lb. steam
Exhaust or low-pressure	6–10 cts. per thousand lb. steam
Steam consumption:	
Topping	78 lb. per bbl.
Topping and cracking	115 lb. per bbl.
Complete processing	250 lb. per bbl.
Percolation filter cleaning	25,000 lb. per thousand cu. ft. filter
Nat. gaso. stripper	1.7–2.5 lb. per gal. gaso.
Fuel required:	
Topping and skimming	7–13.5 per cent crude
Complete processing	15–23 per cent of crude
Heat	419,000–1,190,000 B.t.u. per bbl.
Water:	
Cost of	0.3–2.0 cts. per thousand gal.
Topping	6.6 bbl. per bbl. crude
Topping and cracking	22.3 bbl. per bbl. crude
Complete processing	24.5 bbl. per bbl. crude
Power:	
As pipestill heat, no exchangers	21–37 cts. per million B.t.u.
As pipestill heat, with exchangers	14–30 cts. per million B.t.u.
Electric:	
Topping	0.36 kw.-hr. per bbl.
Topping and cracking	1.31 kw.-hr. per bbl.
Complete processing	3.49 kw.-hr. per bbl.
Total power:	
Topping	1.56 kw.-hr. per bbl.
Topping and cracking	3.17 kw.-hr. per bbl.
Complete processing	5.55 kw.-hr. per bbl.
Cost of electric power	0.4–1.2 cts. per kw.-hr.
Air, cost of	3–7 cts. per thousand cu. ft.

REALIZATION OF CRUDE STOCKS

The most economical "break-up" of products varies day by day because of fluctuations in the market prices and in market specifications. During one season a plant may be most economically operated for the production of maximum yields of gasoline by topping and cracking, whereas at another time the manufacture of a maximum yield of fuel oil or of particular lubricating oils may be advantageous. Consider the posted market prices

Material	Oct. 17, 1933, cts. per gal.	July 3, 1928, cts. per gal.
Gasoline, U.S. motor regular	4¾	7.945
Gasoline, 60–62, 400 E.P. regular	5.0	8.143
Gasoline, 60–62, 400 E.P. premium	5⅜	
Naphtha, 50–52, 450 E.P. blending	4¼	7⅝
Stoddard solvent, 300–410	6⅛	
Lacquer diluent, 140–200	8¾	
Kerosene, 41–43	3½	4¾
Kerosene, 42–44	3⅝	5.0
Furnace oil, 32–36, straw	2⅞	2⅝
Furnace oil, 39–41, prime	3.0	
Gas oil, 32–36, cracking	1⅞	2½
Gas oil, 32–36, 0 to 15 cold test	2¼	
Fuel oil, 28–30, 0 to 10 cold test	2.0	2.0
Fuel oil, 20–22	1.3	1.5
Fuel oil, below 16	1.2	
Petroleum coke, lump, and egg	$7.00*	
Neutral oils, 0 to 10 cold test:		
150 vis., 3 color	7¼	8½†
200 vis., 3 color	9.0	10½†
280 vis., 3 color	12.0	16.0†
400 vis., 4 color	14¾	18 (est.)
Steam-refined cylinder stock 600 light green	6¼	8.0
Brightstock:		
190–200 vis. D	24.0	29.0
150–160 vis., D, 0–10 cold test	22¼	
150–160 vis, D, 25–40 cold test	21¼	22.0
White crude scale, 124–126	3½‡	4.0‡
Crude oil, Okla. and Kans., crude at field, 37 A.P.I	$1.02 per bbl.	$1.31 per bbl.

* Dollars per ton, f.o.b. Chicago refineries.

† Higher cold test.

‡ Cents per pound.

Realization	Per cent, untreated	Per cent, finished	Value at refinery, dollars per bbl.	
			October, 1933	July, 1928
1. Simple topping:				
Gasoline, 60–62, 400 E.P. regular	28*	27.5	0.577	0.939
Kerosene, 42–44	13	12.5	0.19	0.262
Fuel oil, 28 A.P.I	58	58.0	0.487	0.487
Loss (assumed)	1	2.0		
Total	....	....	1.254	1.688
2. Topping through gas oil:				
Gasoline, U. S. motor regular	34	33	0.658	1.110
Kerosene, 41–43	4.5	4.5	0.066	0.088
Gas oil, cracking stock	34	34	0.214 (est.)	0.322 (est.)
Fuel oil, 20–22	26	26	0.142	0.164
Loss (assumed)	1.5	2.5		
Total	....	....	1.080	1.684
3. Topping and cracking:				
Gasoline, 60–62, 400 E.P. premium, cracked	57†	55.0	1.01	2.02 (est.)
Kerosene, st. run 42–44	13	12.5	0.19	0.262
Furnace oil, 39–41 straw	4	4.0	0.050	0.050 (est.)
Fuel oil, 8–9	18	18.0	0.091	0.098 (est.)
Loss and gas	8	10.5	Neglect	
Total	....	....	1.341	2.430
4. Long residuum operation:				
Gasoline, 60–62, 400 regular	28	27.5	0.577	0.939
Kerosene, 42–44	13	12.5	0.19	0.262
Gas oil, 32–36, 0–15 C.T.	25	25.0	0.236	0.276 (est.)
S.R. cylinder stock, 100–120 vis., 600 flash	32	31.0	0.814	1.04
Loss (assumed)	2	4.0		
Total	....	....	1.817	2.517
5. Lubricating oil I (vacuum):				
Gasoline, 60–62, 400 regular	28.0	27.5	0.577	0.939
Kerosene, 42–44	13.0	12.5	0.19	0.262
Gas oil, 32–36, 0 to 15 C.T.	22.0	22.0	0.208	0.243 (est.)
Neutral, 150 vis., 3 color	5.0	5.0	0.152	0.178
Neutral, 400 vis., 4 color	10.0	9.0	0.557	0.68
Brightstock, 190–200 vis, D	16.6	13.3	1.34	1.62
Solid tar (by vacuum)	4.0	4.0		
Loss, sludge, wax, etc	1.4	6.7		
Total	....	....	3.024	3.922
6. Lubricating oil II (vacuum):				
Gasoline, 60–62, 400 regular	28	27.5	0.577	0.939
Kerosene, 42–44	13	12.5	0.19	0.262
Gas oil, 32–36, 0–15 C.T.	22	22.0	0.208	0.242 (est.)
Neutral, 200 vis., 3 color	12	10.2	0.386	0.450
Brightstock, 150–160 vis., D, 0–10 C.T.	20	16.5	1.56	1.66 (est.)
Solid tar (by vacuum)	4	4.0	Neglect	
Loss, sludge, wax, etc	1	7.3	Neglect	
Total	....	....	2.921	3.553
7. Lubricating oil III (residuum):				
Gasoline, 60–62, 400 regular	28	27.5	0.577	0.939
Kerosene, 42–44	13	12.5	0.19	0.262
Gas oil, 32–36, 0–15 C.T.	19	19.0	0.179	0.208 (est.)
Neutral, 150 vis., 3 color	11	9.4	0.286	0.336
Brightstock, 150–160 vis., D, 0–10 C.T.	26	15.8	1.480	1.590 (est.)
Loss, sludge, wax, etc	3	15.8	Neglect	
Total	....	....	2.712	3.335

* Some used to lower initial on kerosene.

† Estimated [Eq. (48)].

for October, 1933,[3] and July, 1928,[4] for Oklahoma, on page 651.

Figure 22 (page 73) is an analysis of a typical 37.3 A.P.I. Mid-Continent crude oil. The yields (Chap. VII) of products from this crude oil and the value of the products per barrel are approximately as shown in the table on page 652.

However, the type or completeness of processing is governed by more factors than the market quotations and the expected yields. Certain crude oils are more suitable for lubricating oil manufacture than others. In fact, some crude oils are so dark that a merchantable long residuum (realization 4) could not be made. Others contain so much wax that 32 to 36 A.P.I., 0 to 15 cold-test gas oil could not be made without undue expense; others are so dark that abnormal quantities of acid would be required; and others contain lubricants of such Viscosity Index that they cannot be marketed. Of even more importance are the market outlets that are available. As an example, few refiners can find a ready market for long residuum or for 190 to 200 viscosity brightstock. However, if a buyer can be located, the manufacture of specialties becomes lucrative.

With the refining costs as generally outlined heretofore, the gross profits for the seven processing realizations are estimated as follows. The gross profit must care for the general administration, depreciation, sales, taxes, and transportation charges.

Realization	Value of products, October, 1933, dollars per bbl.	Approx. operating expenses, dollars per bbl.	Cost of crude (est.)	Gross profit, dollars per bbl.
1. Simple topping.........	1.25	0.15	1.02	0.08
2. Topping through gas oil.	1.08	0.20	1.02	Loss
3. Topping and cracking...	1.34	0.31	1.02	0.09
4. Long residuum.........	1.82	0.33	1.40*	0.09
5. Lubricating oil I........	3.02	0.39	1.40*	1.23
6. Lubricating oil II.......	2.92	0.37	1.40*	1.15
7. Lubricating oil III......	2.71	0.40	1.40*	0.91

* Estimate—Lubricating crude oils are usually purchased by special contract.

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[3] *Oil Gas J.*, Oct. 19, 1933, p. 34.

[4] *Oil Gas J.*, July 5, 1928, p. 148.

The administration, sales, depreciation, etc., expenses will be at least 10 cts. per barrel, and hence operation is unprofitable for the first four break-ups. In addition, the gathering and pipeline charges must be deducted from the gross profits, and this charge may range from 10 to 90 cts. per barrel.

COST OF REFINING EQUIPMENT

In estimating the cost of refinery equipment the preferable method is carefully to design the plant, make an approximate plant layout, and itemize in detail the units of equipment that must be purchased. However, difficulties arise in presenting such a method of cost analysis because the unit cost of steel, brick, labor, machines, etc., varies with the current economic conditions. For this reason the following costs are given on an over-all-capacity basis and are only approximate.

Equipment	Cost of material, labor, and engineering	Range of capacity
Pipestill:		
Distillation	$1,200–$2,100 per million B.t.u. absorbed	50–10 million B.t.u.
Cracking	$1,400–$2,400 per million B.t.u. absorbed	60–15 million B.t.u.
Piping and insulation:		
Topping	$2–$9 per daily bbl.	10,000–1,000 B.P.D.
Vacuum	$4–$9 per daily bbl.	3,000– 500 B.P.D.
Cracking	$5–$10 per daily bbl.	5,000– 500 B.P.D.
Treating plants:		
Inhibitor injection	$0.2–$2 per daily bbl.	
Acid treating	$15–$30 per daily bbl.	
Sweetening	$10–$20 per daily bbl.	
Gray vapor-phase	$15–$25 per daily bbl.	
Furfural extraction	$120–$350 per daily bbl.	4,000– 600 B.P.D.
Copper sweetening, solid	$2 per daily bbl.	
Copper sweetening, solution	$4–$15 per daily bbl.	10,000–1,000 B.P.D.
Topping plants, no treating	$ 16.5–$ 60 per daily bbl.	10,000–1,000 B.P.D.
Pressure distillate rerun	$ 13 –$ 40 per daily bbl.	10,000–1,000 B.P.D.
Vacuum distillation	$ 49 –$ 84 per daily bbl.	3,000– 500 B.P.D.
Solution rerun	$ 38 –$ 68 per daily bbl. of solution	5,000–1,000 B.P.D.
Pressed distillate rerun	$ 39 –$ 72 per daily bbl.	4,000–1,000 B.P.D.
Cracking	$ 70 –$110 per daily bbl.	5,000–1,000 B.P.D.
Wax plant, no rerun	$150 –$200 per daily bbl. wax distillate	1,200– 400 B.P.D.
Centrifuging, no rerun	$600–$1,500 per daily bbl. finished brightstock	600– 100 B.P.D.
Benzene-ketone dewaxing	$125–$360 per daily bbl.	5,000– 500 B.P.D.
Pump house, condenser on top	41–60 cts. per cu. ft. vol.	
Galvanized-iron buildings	25–30 cts. per cu. ft. vol.	
Heat exchangers	$2–$4.5 per sq. ft.	

Costs based on the over-all capacity are of little value in studying the economics of processing. The small items, which constitute the total cost, are necessary if economy is to be practiced. As an example, the cost of generating steam is only a small part of the total processing cost in a refinery. The steam cost may be twice what it should be and yet fail to attract attention, because it constitutes such a small part of the total cost. However, if the boiler house is studied separately, the inefficiency in operation may be clearly apparent.

Although changes in wages and the cost of materials are important, the size of the plant affects the dollars-per-barrel cost much more. Note that a small topping plant may cost $50.00 per barrel daily capacity whereas a 10,000-bbl. plant may cost only $16.50 per barrel.

Such general costs as these must be used with extreme care. The higher of the two costs is due mainly to the small size of the plant rather than to other factors. In prosperous times the costs will all be higher, and during times of business depression the costs may drop far below the figures given.

Kind of Equipment	Rate of Depreciation per Year, Per Cent
Storage tanks	3–5
Stock tanks	5–10
Oil lines	5–8⅓
Sewerage and traps	7–25
Tank cars	4–5
Repair shop and machine tools	8–15
Tools	15–40
Buildings and structures	3–8⅓
Loading racks	7½–10
Pumps and compressors	6¼–15
Boilers	6¼–10
Trucks and automobiles	25–33⅓
Laboratory equipment	20–35
Distillation equipment	8⅓–15
Cracking equipment:	
Complete	10–25
Piping	25–40
Condensers	12½–33⅓
Condenser boxes	5–10
Condenser coils	10–25
Tubular condensers	10–33⅓
Treating tanks, agitators, etc	8⅓–15
Exchangers	6¼–25

Depreciation Rates.—The rate at which equipment is worn out, destroyed by corrosion, or rendered obsolete by technical development is another factor that cannot be accurately computed. The figures shown in the table on page 655 have been used by well-established companies. The tendency of well-established companies has been to depreciate their equipment before it is really useless, and in this manner they have been able to take full advantage of rapid technical advances.

Plant Economy versus Investment.—In the selection of equipment, buyers are often guided too greatly by the initial-investment cost. Particularly in times of depression the refiner needs well designed equipment in order to make a profit. In prosperous times the margin of profit is enough so that even though ineffective processing is practiced, the plant will still show a profit. The plant need not be new or equipped with an array of conveniences, but it must be properly designed and carefully operated. Many highly successful refiners have found it necessary to use old discarded equipment when installing new processes. During poor-profit years these companies have such low investment charges that they can still manage to make a little profit. However, it seldom pays to use an old equipment that is unsuited for the new purpose or to save money on a new equipment by accepting an inadequate design. For example, an apparent saving of about $1,800 might be made in the cost of a bubble-tower (4,000 bbl. per day crude oil) by using 20 rather than 27 plates. If the 27-plate tower recovers an additional one-half of 1 per cent gasoline that otherwise would be sold as kerosene, the saving per year, at a price of 6 cts. for gasoline and 4 cts. for kerosene, would be

$$4{,}000 \times 42 \times 0.005 \frac{(6 - 4)}{100} \times 320 = \$5{,}375 \text{ per year}$$

Thus by a saving of $1,800 in the cost of the tower, a loss of $5,375 of gasoline into kerosene occurred during the first year. In other words, a slight saving in the percentage recovery of products will care for a large investment cost. Likewise, a small saving in labor cost will pay for a large capital investment.

ECONOMICS OF UNIT OPERATIONS

In the following part of the chapter, the economics of several of the most useful unit operations will be discussed as illustrations.

As inferred heretofore, the most successful manner of effecting economies is to study each phase or operation of the complete processing scheme independently. By this manner of approach, savings of such magnitude that they may be unnoticed in the total processing cost are forcefully brought to attention. Only a few illustrations can be given here, but almost all phases of design may be studied by means of economic balances of income versus cost of equipment or its operation. Among such studies are (1) the optimum relation between tower diameter and tray-spacing for a bubble-tower, (2) the optimum thickness of heat insulation, (3) the optimum cost of protective coatings for pipelines, etc., (4) the optimum dimensions of a storage tank or pressure vessel, (5) the optimum spacing between a series of structural beams, (6) the most economical relation between amount of steam and vacuum to use in a vacuum plant, (7) balance of investment for storage vessels versus loss of light ends by evaporation,[5] (8) gravity of crude oil versus cost of processing,[6] (9) separate topping and cracking versus combination operation,[7] (10) invest-

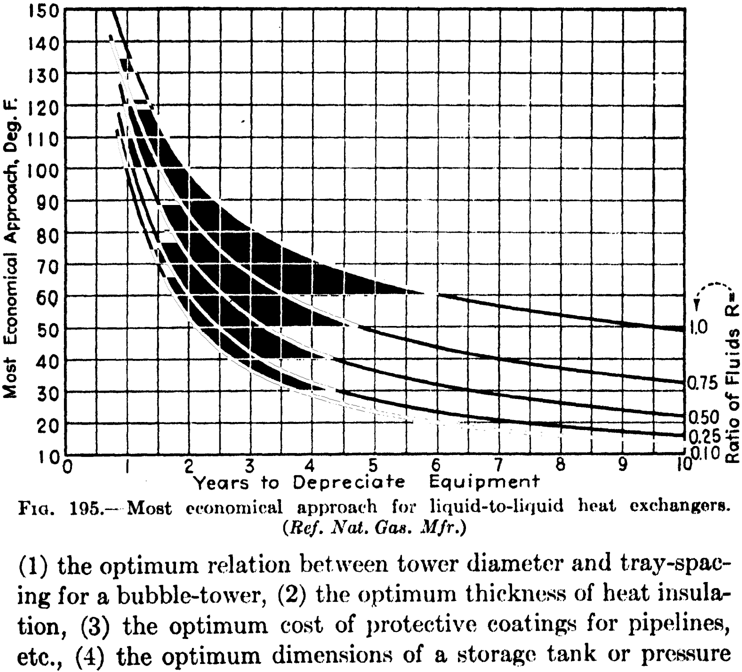

FIG. 195.—Most economical approach for liquid-to-liquid heat exchangers. (*Ref. Nat. Gas. Mfr.*)

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[5] FRANKLIN, W. B., Storage of Light Ends, *Ref. Nat. Gaso. Mfr.*, June, 1937, p. 277.

[6] NELSON, W. L., *Ref. Nat. Gaso. Mfr.*, December, 1936, p. 572.

[7] CHAMBERLAIN, N. F., *Ref. Nat. Gaso. Mfr.*, December, 1937, p. 571.

ment in natural-gasoline plant versus oil-gas ratio,[8] (11) cost of cracking plant versus gravity of charge-stock,[9] (12) life of corrosion-resistant materials (tubing) versus cost,[10] and (13) coking versus cracking as a means of disposing of residues (page 528).

Economics of Heat-exchange.—The net saving effected by the recovery of waste heat approaches a definite limit in any plant equipment. The value of the heat saved, less the cost of the equipment and the cost of operating the equipment, is the net saving. This approaches a high value for a particular set of conditions and decreases if any of the conditions are changed.

In selecting heat exchangers an important consideration is the most economical "approach" or difference in temperature between the incoming cooling medium and the outgoing heating medium. The maximum recovery of heat occurs if these two streams are at the same temperature, but in practical heat-exchange equipment a difference in temperature must exist.

For liquid-to-liquid exchangers, the relationship among the value of heat, cost of surface, magnitude of the heat-transfer rate, and the several other variables that govern the most economical approach is extremely complicated—but for a particular refinery situation all the variables have fixed values and the relationship is reasonably simple. For the following values of variables the most economical approach[11] behaves as indicated in Fig. 195:

Difference in temperature between the 2 incoming fluids	200°F.
Cost of heat-exchanger surface	$2.66 per sq. ft.
Interest rate	6 per cent
Cost of upkeep and repair for each million B.t.u	$160 per year
Value of fuel, per million B.t.u	17 cts.
Heat-transfer rate	25

In this figure, the most economical approach is given in degrees Fahrenheit and the factor labeled R is the ratio of the weight of the larger of the two fluids to the weight of the smaller-quantity fluid.

Cost of Pipestill Heat.—The over-all economy of installing exchangers involves other parts of the plant equipment as well as the exchangers themselves. If exchangers are installed in conjunction with a pipestill, a smaller still may be required because less heat is absorbed in the still but the flue gases will leave at a higher temperature and hence more heat will be lost in the gas. At the same time, less cooling surface and less cooling water will be required for the condensers and coolers of the plant, because the products are partly cooled by heat-exchange. The particular amount of heat-exchange that is economical may be determined by comparing the total costs of absorbing heat in the pipestill and exchangers and then removing it again in the coolers. Costs of generating heat in a 20,000,000-B.t.u. simple pipestill distillation unit are approximately as follows:

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[8] NISSON, A. H., *J. Inst. Petroleum Tech.*, **24**, 69 (1938).

[9] NELSON, W. L., *Oil Gas J.*, Apr. 6, 1939, p. 55.

[10] NELSON, W. L., *Oil Gas J.*, June 3, 1937, p. 97; and June 24, 1937, p. 79.

[11] NELSON, W. L., Economics of Heat Exchanger Design, *Ref. Nat. Gaso. Mfr.*, August, 1936, p. 293.

Pipestill	Cents per million B.t.u.	Saving, dollars per year
Without exchangers	23	
With exchange to 300°F.	17.3	7,220
With exchange to 500°F.	14	13,820
With exchange to 550°F.	14.6	13,200

In this particular case it is not economical to heat the oil by exchangers to a temperature higher than 500°F.

In general, the efficiency for a pipestill should not be so high as for a boiler. Oil is usually at 300 to 500°F. before it enters the pipestill, but the feed-water for a boiler may enter the economizer at a temperature as low as 60°F. Thus a pipestill operates most economically at an efficiency of 70 to 75 per cent, but a boiler may operate at 80 to 85 per cent.

The flue gases should leave the pipestill at a temperature about 300°F. higher than the charge-stock temperature. A closer approach requires a much larger convection section, and a larger approach allows such a large heat loss to the stack that the expenses again rise. These relations are illustrated in Fig. 196. The figure was computed for a radiant type of pipestill absorbing about 10,000,000 B.t.u. per hour, fuel cost 40 cts. per barrel, and depreciation in 6 years at an interest rate of 6 per cent.

Although a saving of ½ ct. per million B.t.u. does not sound large, it amounts to about 3.5 per cent of the cost of generating heat and for a 20,000,000-B.t.u. still amounts to $1,500.00 per year.

The optimum velocity for flue gases in the convection section of a still can be computed in a similar manner. As the velocity is increased, the surface in the convection section becomes smaller but the friction loss becomes greater, and a taller stack must be provided. These factors affect the cost of the convection section and stack as indicated in Fig. 197.

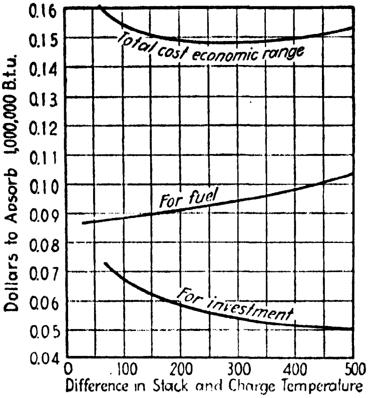

FIG. 196.—Most economical stack-gas temperature for a pipestill.

Practical Recovery for Absorption Plant.—The yield of natural gasoline that is produced in a gasoline plant is directly related to the pentane-plus content of the gas and to the amount of pentane-plus that is recovered. Thus, designers have tended to build plants that would recover 99 per cent of the pentane contained in the gas. This practice, however, is not usually economical, because the cost of operation mounts rapidly as more than 85 per cent of the pentane is recovered, so that in general it may cost twice as much to recover 99 per cent as to recover 85 per cent of the pentane. The variables such as cost of oil recirculation, value of the gasoline product, and cost of stabilizing the gasoline

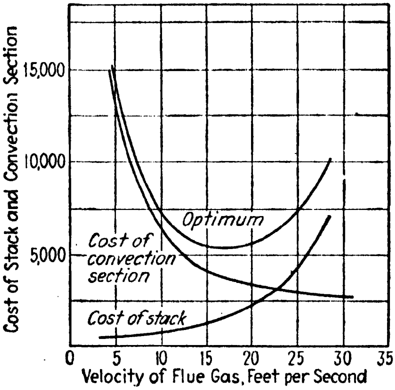

FIG. 197.—Most economical flue-gas velocity in convection section of pipestill.

are related[12] in such a way that the loss involved in recovering 99 per cent of the pentane is somewhat as shown in Table 103. Note that the most economical recovery is also given in the table.

TABLE 103.—LOSS BY OPERATION AT 99 PER CENT RECOVERY OF PENTANE

Pressure, lb. per sq. in.	Pentane-plus, per cent	Grade of gasoline	Gasoline price, cts. per gal.	Most economical recovery, per cent	Loss, cts. per 1,000 cu. ft. by operating at 99 per cent recovery
50*	7	22–70	4	94.25	1.287*
50	3	30–70	2	89.8	0.821
50	3	30–70	4	94	0.577
50	3	14–55	4	92	0.455
50	9	14–55	4	96.2	0.286
50	9	30–70	4	97.4	0.227
400	3	14–55	4	96.4	0.117
400	3	30–70	4	97.5	0.068
400	9	30–70	4	98.9	Nil

* Refinery conditions, oil recirculation cost of 0.1 cts. per gal.

The conditions used in computing Table 103 were

Cost of oil recirculation	0.05 cts. per gal. oil
Cost of stabilizing gasoline	0.13 cts. per gal.
Molecular weight of oil	190
Specific gravity of oil	0.84

Dimensions of Pipestills.—Immature designers are usually confused in deciding what should be the dimensions of a pipestill, whereas experienced designers have become accustomed to using certain arrangements that in some instances may be needlessly expensive. The economic relationship among the costs of tubes, bends, tube supports, roof, walls, etc., is exceedingly complicated. Nevertheless, cost equations can be derived for any conventional type of still such as rear convection or center convection. Figure 198 shows the most economical tube length[13] versus the total cost of pipestills of the overhead convection type shown in Figure 133 (page 432). In general, the high cost of return bends as against the cost of tubing, supports, walls, etc., calls for

[12] NELSON, W. L., *Ref. Nat. Gaso. Mfr.*, May, 1936, p. 167.

[13] NELSON, W. L., *Oil Gas J.*, May 11, 1939, p. 63; and June 1, 1939, p. 34.

longer tubes than have commonly been used. This tendency is becoming evident in stills designed during the last few years.

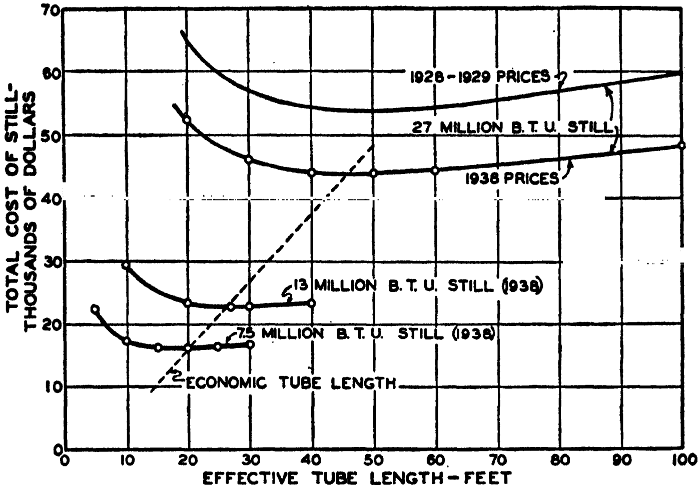

FIG. 198.—Most economical tube length for overhead convection type pipestills. (*Oil Gas J.*)

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CHAPTER XXX

TYPICAL DESIGN CALCULATION

The design of petroleum equipment is made difficult by the complex composition of petroleum oils. Many features of a design defy exact computation, and such cases must be met by the judgment and experience of the design engineer. The factors of judgment and experience cannot be completely eliminated, and hence the success of the design depends, to a large degree, upon the experience of the designer.

These are the facts concerning the design of petroleum equipment. However, successful equipment can be designed, even though the calculations are not perfect, because a well-designed plant can be operated to overcome the inadequacies in the design information.

Outline of Computations.—In this chapter a continuous pipestill topping plant will be designed. A more complicated plant would be more interesting to many engineers, but the calculations would be so involved that they would be almost useless to most readers.

TABLE 104.—YIELDS AND PROPERTIES OF PRODUCTS

Material	Per cent	A.P.I.	Notes
Loss*.................	0.5	....	About 7 cu. ft. of gas per bbl. (Table 87)
Gasoline...............	31.0	60.2	A.S.T.M. end-point about 392 (Fig. 28)
Kerosene..............	10.0	43.0	A.S.T.M. end-point about 493 (Fig. 28)
Gas oil.................	26.0	34.9	By difference
Reduced crude.........	32.5	22.5	Viscosity at 210°F., about 107 (Fig. 199)
Crude.................	100.0	38.6	Fig. 199

* Consider as a gas which has a molecular weight of 45.

The Mid-Continent crude oil shown in Fig. 199 is to be topped for the production of gasoline, kerosene, gas oil, and reduced crude oil, as shown in Table 104. Its characterization factor is 12.

Obviously, the selection of products depends upon the market demands and sales opportunities that are available. Although products having particular specifications must be produced in the unit, the designer has little need for more detailed specifications than the general information given in Table 104. However, the designer can build a flexible plant and thus permit the plant operator to produce any reasonable specifications that may be desired.

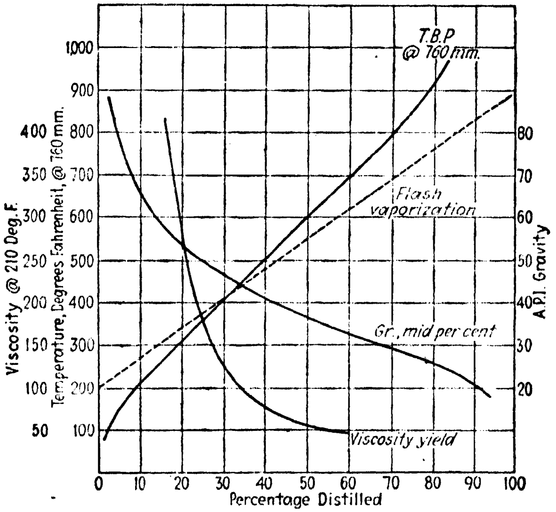

FIG. 199.—Mid-Continent crude oil—38.6 A.P.I.

The design computations can be organized somewhat as follows:

1. Obtain a list of the desirable products from the plant management or the marketing department.
2. Obtain a comprehensive laboratory evaluation of the stock. An analysis, such as shown in Fig. 199, is satisfactory, but if possible the desired products should be produced in the laboratory and examined by routine tests. This is not always convenient, because many combinations of products may be contemplated.
3. Analyze the evaluation curves of the stock for the yields of products, and if possible produce and examine the products in the laboratory (Chaps. V, VI, VII and IX).

4. Prepare a table of the quantities, weights, and oft-used properties of the several stocks (Table 105).
5. Prepare a tentative flow diagram of the process. This may be modified as the design progresses to meet unforeseen conditions (Fig. 200).
6. Design the fractionating tower, determining tower temperatures and diameter.
7. Design heat-exchange system by an economic study of each exchanger. Compute the temperature of the stock as it arrives at the pipestill.
8. Design the pipestill.
9. Design the condensers, coolers, stripper, etc.
10. Estimate steam, water, and power requirements.

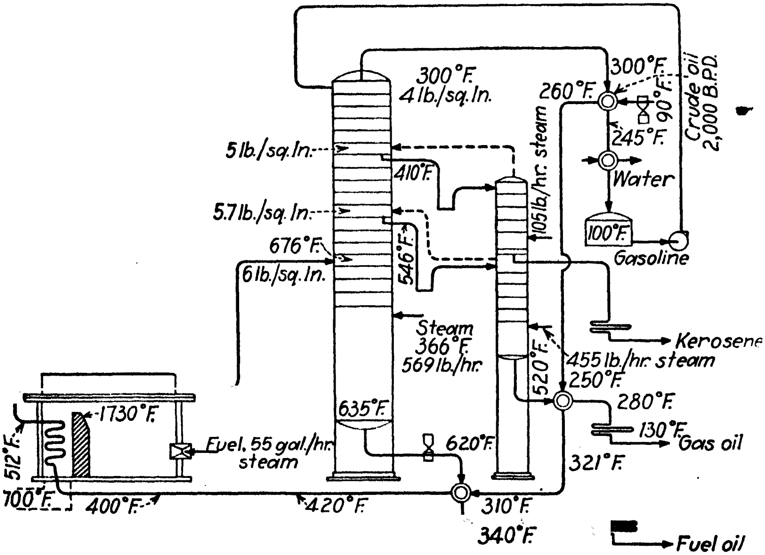

FIG. 200.—Diagram of topping plant.

In a complete computation of this kind, many figures are used over and over again in the computations. Time and confusion may be avoided by tabulating these figures, as in Table 105, at the start of the work.

The general conditions are as follows:

Capacity	2,000 bbl. per day
Temperature of crude oil	90°F. (ave.)
Temperature of cooling water	75°F. (ave.) to 95°F. (max.)
Steam pressure	150 lb. per sq. in. gage; saturation temperature, 366°F.
Corrosion	The crude is classed as a sweet oil and contains only 0.1 per cent sulfur

The flow diagram of the process is shown in Fig. 200. This diagram shows only the major items of equipment, and it is not intended to indicate anything concerning the size or mechanical design of the equipment.

TABLE 105.—USEFUL QUANTITIES AND PROPERTIES
2,000 bbl. per day

Material	Per cent	A.P.I.	Lb. per gal.	Gal. per hr.	Lb. per hr.	50 per cent boiling-point, deg. F.	Molecular weight†
Loss	0.5	....	0.119*	17	70‡	...	45
Gasoline	31.0	60.2	6.14	1,085	6,660	258	116
Kerosene	10.0	43.0	6.75	350	2,360	460	192
Gas oil	26.0	34.9	7.08	910	6,450	635	290
Reduced crude	32.5	22.5	7.65	1,138	8,710		
Crude	100.0	38.6	6.93	3,500	24,250		

* Density, pound per cubic foot at 60°F.

† Fig. 35.

‡ $\frac{2{,}000 \times 7}{379} \times \frac{45}{24} = 70.$

FRACTIONATOR SYSTEM

The design of the fractionation system may be outlined as follows:

1. Draw the flash-vaporization curve of the crude oil unless this curve is included in the laboratory analysis (Figs. 75, 76).
2. Estimate the amount of steam required for stripping.
3. Estimate the temperatures and pressures at all important points in the tower. Adopt the number of plates to be used between cuts (page 504).
4. Compute a heat-balance, and determine the amount of reflux.
5. Compute the diameter of the tower.

The flash-vaporization curve was computed as follows (Figs. 76 and 199):

$$\begin{array}{lll}
\text{70 per cent on T.B.P. curve} & = & 788°\text{F.} \\
\text{10 per cent on T.B.P. curve} & = & \underline{204°\text{F.}} \\
 & & 584°\text{F.}
\end{array}$$

Slope of T.B.P. curve = $^{584}/_{60}$ = 9.73
Slope of flash curve (Fig. 76) = 7.0
50 per cent on T.B.P. = 598°F.
50 per cent on flash curve (Fig. 76) = 550°F.
100 per cent on flash curve = 550 + 50 × 7 = 900°F.
0 per cent on flash curve = 550 − 50 × 7 = 200°F.

This curve is plotted as a straight-line vaporization curve in Fig. 199. With freak stocks, the curvature of the flash curve should be computed as explained in Example 43.

The amount of steam that will be required to strip the kerosene, gas oil, and reduced crude oil can be estimated from the figures given on page 372. Table 106 summarizes the steam quantities.

TABLE 106.—STEAM FOR STRIPPING

Material	Lb. steam per gal.	Gal. per hr. of material	Lb. steam per hr.
Kerosene	0.3	350	105
Gas oil	0.5	910	455
Reduced crude	0.5	1,138	569
Total	...	.....	1.129

The number of plates can be estimated from the tabulation on page 504. The following number of plates will be used:

	No. of Plates
Gasoline to kerosene	6
Kerosene to gas oil	5
Gas oil to vaporizer	3
No. of plates above vaporizer	14
Stripping plates	4
Total no. of plates	18

The pressure at the top of the topping tower is seldom more than 4 lb. per square inch gage. The pressure-drop per plate is discussed on page 479. The pressures in the tower and the amount of steam at various points will be approximately as follows:

Position	Pressure,* lb. per sq. in.	Lb. steam
At top plate	4	1,129
At kerosene plate	5	1,024
At gas oil plate	5.7	569
At vaporizer	6.1	569

* Top velocity approximately 2.0 ft. per second (see computed velocity, page 672).

Vaporizer Temperature.—The vaporizer temperature, as obtained from the flash curve at 760 mm., must be corrected for the tower pressure and for the effect of steam. The gasoline, kerosene, gas oil, and loss amount to 67.5 per cent.

Vaporizer temperature at 760 mm. (flash curve)...... 670°F.

Pressure at vaporizer....... $760 + \frac{6.1}{14.7} \times 760 = 1{,}075$ mm.

Mols of gasoline (Table 105)............ $\frac{6{,}660}{116} = 57.5$

Mols of kerosene..................... $\frac{2{,}360}{192} = 12.3$

Mols of gas oil...................... $\frac{6{,}450}{290} = 22.2$

Total mols vapor.......................... $= 92.0$

Mols steam........................... $\frac{569}{18} = 31.6$

Total mols vapor and steam.................. 123.6

$$\text{Partial-pressure of oil} = \frac{92}{123.6} \times 1{,}075 = 801 \text{ mm.}$$

Vaporizer temperature at tower conditions, by correcting 670°F. to 801 mm. by means of Fig. 52, is 676°F.

Tower Temperatures.—This tower, the stock that is being processed, and the quantities of steam are normal. Under these conditions, the side-draw temperatures may be estimated from Fig. 146. In cases in which the conditions are not normal, the method outlined in Example 71 must be used.

The tower temperatures and the corresponding latent heats are approximately as follows:

	Deg. F.	Latent heat†
Top temperature.........	300*	123
Kerosene drawplate......	410	109
Gas oil drawplate........	546	92
Bottoms product.........	635	

* Check later (see page 671).

† Fig. 37.

The bottoms temperature cannot be estimated as accurately as the other temperatures. However, it is not of great importance because it does not properly belong in the tower balance and is only included there as a factor of safety. Most of the cooling of the bottoms material in the tower is caused by these factors:

1. Vaporization of a part of the bottoms by steam.
2. Heat losses through the tower shell.
3. Heat used to raise or lower the temperature of the steam.

Table 35 (page 247) indicates that the liquid material from the vaporizer contains about 10 per cent of material that boils below the flash temperature. The vaporization of this 10 per cent of material uses some heat, but the greater part of the cooling is due to the other two factors. The cooling due to vaporization can be computed by balancing the heat of vaporization against the sensible heat loss that it causes; the cooling (or heating) due to steam may be computed by a heat-balance; and the cooling due to losses through the walls of the tower can be computed by the resistance theory as given in Examples 35 and 38. For this tower the cooling of the bottoms product is approximately as follows:

	Deg. F.
Due to vaporization	12
Due to heat losses	13
Due to heating of steam	15

Thus the *bottoms temperature* is approximately 636°F.

HEAT-BALANCE OF TOWER

Temperature datum, vaporizer temperature or 676°F. (Figs. 33, 34)

		B.t.u. per Hr.
Cooling gaso. (vap.)	6,660(676 − 300)0.59 =	1,480,000
Cooling kero. (vap.)	2,360(676 − 410)0.6 =	376,000
Cooling gas oil (vap.)	6,450(676 − 546)0.63 =	530,000
Cooling reduced crude* (liq.)	8,710(676 − 635)0.77 =	275,000
Cooling steam*	1,129(366 − 300)0.5 =	37,000
Total sensible heat		2,698,000
Condense kero	2,360 × 109 = 258,000	
Condense gas oil	6,450 × 92 = 593,000	
Total latent heat	851,000 =	851,000
Reflux heat		3,549,000

---

* Actually, these heats have already been accounted for in computing the bottoms temperature, but most designers include them as a factor of safety. If they are not included, then the bottoms temperature should be considered as 676°F. and the steam temperature as 676, 410, and 546°F. for the amount of steam that enters the system at the vaporizer, kerosene plate, and gas oil plate respectively.

With the reflux available at 100°F., the amount of cold reflux per hour is

Lb. cold reflux............. $\dfrac{3,549,000}{123 + (300 - 100)0.58} = 14,850$

Gal. cold reflux................. $\dfrac{3,549,000}{239} \times \dfrac{1}{6.14} = 2,420$

Gal. cold reflux per gal. product............ $\dfrac{2,420}{1,085} = 2.23$

Check on top temperature:

Mols reflux and product......... $\dfrac{14,850 + 6,660}{116} = 186$

Mols steam............................ $\dfrac{1,129}{18} = 63$

Total mols.................................. $\overline{249}$

Partial-pressure....... $\dfrac{186}{249} \times \left(760 + \dfrac{4 \times 760}{14.7}\right) = 723$ mm.

The 100 per cent point on the flash-vaporization curve of the gasoline is approximately 315°F. When corrected to 723 mm., the temperature is about 312°F. However, by Table 69 the computed top temperature is usually about 3 per cent high. Hence the top temperature would be 312 × 0.97 = 302°F. The assumed top temperature was 300°F., and this is a satisfactory check.

Diameter of Tower.—The allowable mass velocity of the vapors at the top of the tower can be computed from Eq. (82). The constant C can be obtained from Fig. 150. At a tray spacing of 22 in., which allows a manhole on each tray, the value of C is about 590.

The density d_1 of the gasoline at 300°F. may be obtained from Fig. 43:

$$\begin{aligned} \text{Sp. gr. at } 60 &= 0.738 \\ \text{Sp. gr. at } 300 &= 0.632 \\ d_1 = 0.632 \times 62.4 &= 39.4 \text{ lb. per cu. ft.} \end{aligned}$$

The density d_2 of the vapor at 300°F. and 4 lb. gage will be computed by the perfect gas laws:

		Mols	Lb.
Internal reflux...............	$\dfrac{3,549,000}{123 \times 116} =$	249	28,800
Gasoline product......................	$=$	57.5	6,660
Steam..........................	$\dfrac{1,129}{18} =$	62.7	1,129
Total at top..........................		$\overline{369.2}$	$\overline{36,589}$

$$\text{Volume at top} = 369.2 \times 379 \times \frac{760}{520} \times \frac{14.7}{18.7} = 161{,}000 \text{ cu. ft. per hr.}$$

$$d_2 = \frac{36{,}589}{161{,}000} = 0.221 \text{ lb. per cu. ft.}$$

$$\text{Mass velocity } W = 590[0.221(39.4 - 0.221)]^{0.5} = 1{,}730 \text{ lb. per sq. ft. per hr.}$$

Cross-sectional area of tower.......... $\frac{36,589}{1,730} = 21.0$ sq. ft.
Factor for overcapacity..................... 2.5
Area used.............................. 23.5 sq. ft.

Use a diameter of 5 ft. 6 in.

This corresponds to a linear velocity of $\frac{161,000}{23.5 \times 3,600} = 1.9$ ft. per sec.

HEAT-EXCHANGE SYSTEM

The number of products that may be used to heat the charge-stock is an economic problem. It usually pays to install condensing exchangers for the overhead product and reflux, because of the large quantity of heat that is available in these materials and because the transfer rate is relatively high in condensing equipment. In the case of kerosene, an exchanger may not be economical because the kerosene stream is small and the cost per unit of surface rises. Heat exchangers are generally used on the gas oil stream and other high-boiling distillate streams because of the high temperature. The same holds true for the bottoms product, except that the viscosity may be so high that an exchanger is not economical and because such stocks often contain suspended solid matter. Bottoms exchangers are not usually used for viscous stocks unless a pump is provided for the bottoms product.

In general, the exchangers are purchased from manufacturing companies, and these companies are asked to design the exchange-system. However, the plant engineer must not depend entirely on the computations from these manufacturers. For this reason, the following approximate design of the heat-exchange system is suggested.

The feed-stock should be routed through the exchangers as follows:

1. Gasoline and reflux condenser exchanger.
2. Kerosene exchanger.
3. Gas oil exchanger.
4. Reduced crude oil exchanger.

The temperatures in these exchangers will be developed during the computations and are shown in Fig. 201.

Gasoline Condensing Exchanger.

Lb. of gasoline and reflux = 14,850 + 6,660 = 21,510
Lb. of steam = 1,129

Using an approach of 40°F. on the hot end of the exchanger, the heat that can be absorbed is

$$24{,}250(260 - 90)0.52 = 2{,}140{,}000 \text{ B.t.u. per hr.}$$

This amount of heat will condense about half of the gasoline and reflux and require an outlet temperature, for the gasoline, of about 245°F.

A check on the amount of heat that is removed follows:

Cool half of vapor and the condensate from it	$\frac{21{,}510}{2}(300 - 245)\frac{0.63 + 0.48^*}{2} =$	331,000
Cool vapor that does not condense	$\frac{21{,}510}{2}(300 - 245)0.475 =$	281,000
Cool steam	$1{,}129(300 - 245)0.5 =$	31,000
Condense half of vapor	$\frac{21{,}510}{2} \times 128 =$	1,380,000
		2,023,000

* Average specific heat of vapor and liquid.

This check is sufficiently close.

Transfer Coefficients.—The crude oil will pass through the tubes, and a velocity of 4 ft. per second will be possible because of the pressure that is available.

The average film-temperature of the crude oil will be about 220°F. The viscosity of the crude oil, at this temperature is about 2 (Fig. 48). Film transfer rate for crude oil, in 1-in. tubes, is about 185 (Fig. 125).

The gasoline, reflux, and steam will be cooled on the outside of the tubes. The condensing coefficient will be about 140 (Table 56).

The approximate fouling conditions are as follows:

Crude in tubes	5.0 (Fig. 128)
Gasoline in shell	1.0
Total fouling factor	6.0

Over-all Coefficient.

$$H = \frac{1}{1/185 + 1/140 + 0.006} = \frac{1}{0.0173} = 54$$

Larger temp. diff. = about 155

Smaller temp. diff. = about 40

Log mean temp. diff. (Fig. 65) = 85°F.

$$\text{Surface} = \frac{2{,}140{,}000}{85 \times 54} = 466 \text{ sq. ft.}$$

Factor for overcapacity = 64 sq. ft.

Use 530 sq. ft.

Kerosene Exchanger.—This exchanger may not be economical because of the small amount of kerosene and because the crude oil is now at about 260°F. The crude oil will be cooled a little between exchangers, and the kerosene will be cooled a little by the stripper.

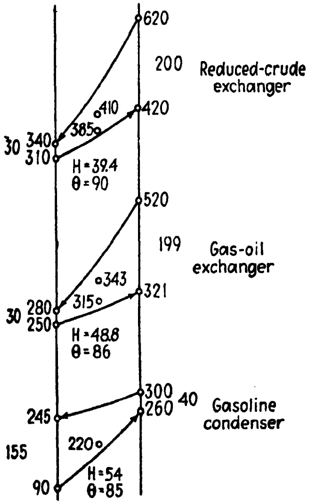

FIG. 201.—Temperatures in heat-exchange system.

Oil	Lb.	Approx. temp.
Kerosene...........	2,360	385
Crude.............	24,250	250

An approximate design was made, showing that the exchanger would be very small and would cost about $400. It would hardly pay for itself in two years, and this fact, along with its small size, indicates that it would not be a good investment.

Gas Oil Exchanger.

Oil	Lb.	Approx. temp. after stripper, etc.
Gas oil.	6,450	520
Crude.	24,250	250

Using an approach of 30°F., the amount of heat that is exchanged is about as follows:

$$\underset{\text{Gas oil}}{6{,}450(520-280)0.645} = \underset{\text{Crude oil}}{24{,}250(321-250)0.58} = 1{,}000{,}000 \text{ B.t.u.}$$

log mean temp. difference = 89°F.

The transfer-rate conditions will be about as follows:

Oil	Approx. film. temp.	Viscosity*	Side	Approx. velocity	Film rate†	Fouling factors
Gas oil.	343	0.85	Shell	1	87	2
Crude.	315	0.56	Tube	4	335	4

* Fig. 48.

† Figs. 125 and 126.

$$H \text{ for gas oil exchanger} = \frac{1}{1/87 + 1/335 + 0.006} = 48.8$$

$$\text{Surface} = \frac{1{,}000{,}000}{89 \times 48.8} = 230 \text{ sq. ft.}$$

$$\text{Factor for overcapacity} = \underline{35}$$

$$\text{Use } 265 \text{ sq. ft.}$$

Bottoms Exchanger.

Oil	Lb.	Approx. temp.
Reduced crude.	8,710	620
Crude.	24,250	310

Many plant men contend that bottoms exchangers give more trouble than they are worth. If the bottoms stock is dirty or the exchanger is not periodically cleaned, then this is doubtless true, but under proper conditions and with careful supervision bottoms exchangers can be successfully used. In this case a bottoms exchanger would doubtless be justified.

Using an approach of 30°F., the duty of the exchanger would be

$$\underset{\text{Reduced crude oil}}{8{,}710(620-340)0.69} = \underset{\text{Crude oil}}{24{,}250(420-310)0.627} = 1{,}680{,}000 \text{ B.t.u.}$$

log mean temp. diff. (Fig. 65) = 90°F.

The transfer-rate conditions will be about as follows:

Oil	Approx. film temp., deg. F.	Viscosity	Side	Approx. velocity	Film rate	Fouling factors
Reduced crude......	410	2.3	Shell	2*	103	10
Crude.............	385	0.4	Tube	4	365	3
						13

* Pump on reduced crude oil.

$$H = \frac{1}{1/103 + 1/365 + 0.013} = 39.4$$

If the reduced crude oil were not handled by a pump, the overall rate would be only about 26.

$$\text{Surface} = \frac{1{,}680{,}000}{90 \times 39.4} = 475 \text{ sq. ft.}$$

$$\text{Factor for overcapacity} = \underline{\ 65\ }$$

$$\text{Use } 540 \text{ sq. ft.}$$

Water Coolers and Condensers.—The design of these equipments is much the same as for the exchangers, and hence only one cooler, the gas oil cooler, will be designed. A tubular type of cooler will be used.

The gas oil is available at 280°F. from the exchanger, and it will be cooled a few degrees in the transfer line. However, the cooling will be neglected and considered as a further factor of safety. The flash-point of the gas oil will be above 160°F., and hence it need not be cooled to lower than about 130°F. The water will be sent through the tubes. It will not be heated to over 125°F. because scale may be deposited.

Duty of Gas Oil Cooler.

$$\underset{\text{Gas oil}}{6{,}450(280 - 130)0.53} = \underset{\text{Water}}{W(125 - 95)1.0} = 512{,}000 \text{ B.t.u.}$$

$$W = \text{lb. water} = 17{,}100$$

$$\text{Gal. water} = \frac{17{,}100}{8.33} = 2{,}055 \text{ gal. per hr.}$$

Transfer-rate conditions will be as follows:

	Approx. film temp.	Viscosity	Side	Approx. velocity	Film rate*	Fouling factor
Gas oil.	165	3.7	Shell	1	53	4
Water.	. .	. . .	Tube	5	610	3

* Fig. 126 and Table 55.

$$H = \frac{1}{\frac{1}{53} + \frac{1}{610} + 0.007} = 36.4$$

$$\text{log mean temp. diff.} = 81$$

$$\text{Surface} = \frac{512{,}000}{36.4 \times 81} = 174 \text{ sq. ft.}$$

$$\text{Factor of overcapacity} = \underline{26}$$

$$\text{Use } 200 \text{ sq. ft.}$$

PIPESTILL HEATER

The crude oil will arrive at the pipestill at a temperature of about 410°F. It must be heated to a temperature sufficiently high to vaporize, by flash vaporization, 67.5 per cent of the crude oil. This requires a temperature of about 676°F. at the vaporizer at a pressure of 6.1 lb. per square inch absolute (page 669).

The temperature at the outlet of the still will be somewhat higher than 676°F. because of the adiabatic vaporization that occurs in the transfer line to the tower. The outlet temperature can be computed with fair accuracy, but it is not important and in this case will not be computed.

Pipestill Duty.—In computing the heat that will be absorbed in the pipestill, it is not necessary to know the pressure in the still or the outlet temperature, because the same amount of heat is required by any route, if the initial and final conditions are the same for each route (Examples 30 and 31).

Assume that vaporization of the products occurs at the following arbitrary temperatures because the heat data are most accurate at these conditions and because some of the heat quantities have already been computed. However, the latent heats must be picked accordingly.

Oil	Temperature, deg. F.	Latent heat (Fig. 37)
Gasoline	410	106
Kerosene	410	109
Gas oil	546	92

		B.t.u. per Hr.
Sensible heat:		
Gas*	70(676 − 410)0.68 =	12,600
Gasoline (vap.)	6,660(676 − 410)0.615 =	1,090,000
Kerosene (vap.)	2,360(676 − 410)0.6 =	376,000
Gas oil (liq.)	6,450(546 − 410)0.69 =	605,000
Gas oil (vap.)	6,450(676 − 546)0.628 =	527,000
Reduced crude	8,710(676 − 410)0.7 =	1,620,000
Total sensible heat		4,230,600
Latent heat:		
Gasoline	6,660 × 106 = 706,000	
Kerosene	2,360 × 109 = 258,000	
Gas oil	6,450 × 92 = 594,000	
Total latent heat	1,558,000 =	1,558,000
Total pipestill duty		5,788,600

Consider the gas as a 150 A.P.I. material in estimating specific heat.

Heat-balance of Still.—The approach between the temperature of the stack gas and the temperature of the feed-stock should be about 290°F. (Fig. 196). The stack gas temperature would then be 410 + 290, or 700°F.

The furnace could be fired with 25 per cent excess air, but general operation is nearer 40 per cent excess air. With this amount of excess air and burning some of the reduced crude oil as a fuel, the loss due to the temperature of the stack gases amounts to about 18 per cent (Fig. 56).

The heating operation is not a difficult one, and hence the radiant section can be designed for a radiation factor of 0.45 (Table 50). This corresponds to a radiant-absorption rate of about 30,000 B.t.u. per square foot of projected area per hour (Fig. 137).

The losses through the walls, etc., of the still amount to about 3 per cent from the radiant section and 2 per cent from the convection section (Table 65).

The efficiency of the still is 100 − 18 − 5 = 77 per cent.

The heat-balance of the furnace is about as follows:

Heat quantity	Per cent of net H.V.	Heat, B.t.u. per hr.
Heat input	100	7,510,000
Wall losses	5	376,000
Stack loss	18	1,350,000
Radiant absorption	45	3,380,000
Convection absorption (by diff.)	32	2,404,000

Convection-section.—If all of the gasoline is vaporized in the convection section, the oil is at approximately 512°F. as it leaves the convection section:

$$6660 \times 106 + 24{,}250(x - 410)0.685 = 2{,}404{,}000$$

$$x = 512\text{°F.}$$

The flue gas that enters the convection section still contains 100 − 45 − 3, or 52 per cent, of the net heating value of the fuel. Figure 65 shows that the temperature of the gas at the bridgewall will be approximately 1730°F. The furnace temperature that is recorded in plant operation is lower than this, but it is usually measured at another point.

$$\text{Larger temp. diff.} = 1{,}730 - 512 = 1{,}218$$

$$\text{Smaller temp. diff.} = 700 - 410 = 290$$

$$\text{log mean temp. diff.} = \frac{1{,}218 - 290}{\ln \dfrac{1{,}218}{290}} = 646\text{°F.}$$

The convection section will be designed for an average flue-gas velocity of 15 ft. per second. With tubing that has an outside diameter of 4 inches and with an average flue-gas temperature of about 1120°F., the over-all convection coefficient is about 7.3 (Table 64).

$$\text{Convection surface} = \frac{2{,}404{,}000}{7.3 \times 646} = 510 \text{ sq. ft. outside surface}$$

$$\begin{array}{lr} \text{Factor for overcapacity} & \underline{60} \\ & \text{Use } 570 \text{ sq. ft.} \end{array}$$

Radiant Section.

$$\text{Radiant surface} = \frac{3{,}380{,}000}{30{,}000} = 113 \text{ sq. ft. projected area}$$

$$\begin{array}{lr} \text{Factor for overcapacity} & = \underline{17} \\ & \text{Use } 130 \text{ sq. ft.} \end{array}$$

In computing the tube diameters, the data given in Chap. XXII will be useful. However, the tube layout and structural design of the still will not be given herein because these details are too complicated to be presented in a discussion of this kind.

Fuel Required.—The net heating value of a 22.5 A.P.I. fuel is about 17,800 B.t.u. (Fig. 50 and Table 25).

Fuel

$$\frac{7{,}510{,}000}{17{,}800} = 422 \text{ lb. per hr.}$$

or

$$\frac{422}{7.65} = 55 \text{ gal. per hr.}$$

One burner could be used, but two small ones would be more satisfactory.

Steam for atomizing (Fig. 58),

$$422 \times 0.3 = 127 \text{ lb. per hr.}$$

WATER REQUIRED

The several products leave the coolers at almost the same temperature as the crude oil enters the plant, and hence the heat that must be removed by cooling water is almost equal to the heat that is added to the oil in the pipestill. When the water is at its maximum temperature of 95°F.,

$$\text{Approx. gal. of cooling water} = \frac{5,788,600}{(125 - 95)8.33} = 23,200 \text{ gal. per hr.}$$

This is a maximum figure because some of this heat is lost through the insulation of the equipment.

STEAM REQUIRED

Reciprocating steam pumps would be used for the charge-stock and the reduced crude oil. The steam required for these pumps would be guaranteed by the pump manufacturers, but simple approximations can be had, as follows:

The charge pump will operate at a pressure sufficiently high to force the oil through the exchangers and the pipestill and into the fractionating tower. The charge-pressure will be about 160 lb. per square inch gage.

A simple manner of getting the steam consumption of a pump is to consider that the volume of oil that is pumped is the same as the volume of steam that is required if the pressures are the same, and except for the inefficiency of the pump. If the pressures are not the same, then the volume of steam that is used will be inversely proportional to the pressure. In this manner, the approximate steam consumption at an over-all efficiency of 50 per cent is as follows:

The specific volume of 150-lb. gage pressure steam is 2.76.

$$\frac{3,500}{7.5} \times \frac{160}{150} \times \frac{1}{0.5} \times \frac{1}{2.76} = 360 \text{ lb. per hr.}$$

In a similar manner the steam required for the bottoms pump, when pumping at 40 lb. per square inch, is about

$$\frac{1,138}{7.5} \times \frac{40}{150} \times \frac{1}{0.45} \times \frac{1}{2.76} = 32.5 \text{ lb. per hr.}$$

APPROXIMATE STEAM REQUIREMENTS

	Lb. per hr.
For pumps	382
For stripping (process steam)	1,129
For burners	127
Total	1,638

With the feed-water at 130°F. and with saturate 150-lb. gage steam, the boiler horsepower corresponding to 1,638 lb. per hour is about 54.

Summary.—The design as herein presented is inadequate in many respects. However, each design depends greatly upon the particular plant conditions that are encountered and upon a multitude of practical details. These details cannot be presented without becoming involved in a hopelessly tedious discussion and one that would be uninteresting to most readers.

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